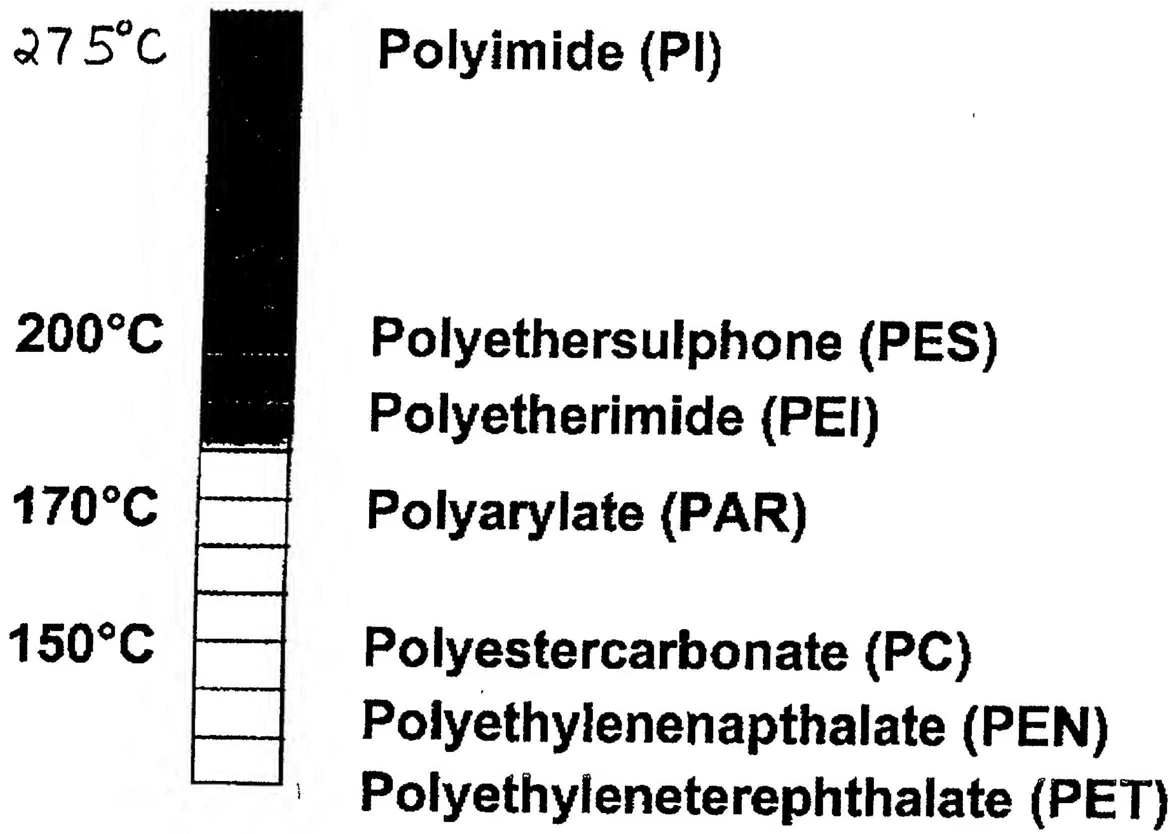
275°C
200°C
170°C
150°C
Polyimide (PI)
Polyethersulphone (PES)
Polyetherimide (PEI)
Polyarylate (PAR)
Polyestercarbonate (PC)
Polyethylenenapthalate (PEN)
Polyethyleneterephthalate (PET)

Appendix A

EMERGING TRANSPARENT CONDUCTING OXIDES FOR ELECTRO-OPTICAL APPLICATIONS

CHARACTERISTICS OF EMERGING TCO MATERIALS

Material	Transmittance (%)	Resistivity ($x10^{-4}\Omega cm$)	Carrier Concentration ($x10^{20}cm^{-3}$)	Mobility ($cm^2/V^{-1}s^1$)	Film Thickness (nm)	References
$CdSn_2O_4$	88	1.2	9.0	59.6	530	Wu, X.et al, JVST A 15(3),1997
$CdGa_2O_4$		83	10			Omata,T.et al Appl. Phys Lett 62 (5) 1993
$CdIn_2O_4$	90	2.3	6.1	44.2	290	Wu, X.et al, JVST A 15(3),1997
$CdSb_2O_6$ (Y)	90	240	1.3	1.9	170	Yanagawa,K.et al Appl. Phys. Lett. 65(4) 1994
Cd_2GeO_4	98 (Internal)	1000	0.1	5		Hosono, H.etal Appl. Phy. Lett 67(18)1995
ITO	91	1-2	10	37	140	Heiz,b.,OIC Topical Meeting, 1998

Appendix B

EMERGING TRANSPARENT CONDUCTING OXIDES FOR ELECTRO-OPTICAL APPLICATIONS

CHARACTERISTICS OF EMERGING TCO MATERIALS

Material	Transmittance (%)	Resistivity ($x10^{-4}\Omega cm$)	Carrier Concentration ($x10^{20}cm^{-3}$)	Mobility ($cm^2/V^{-1}s^{-1}$)	Film Thickness (nm)	References
ZnO(Al)	90	1.4	9.9	45	150	Imaeda, K.et al 43rd AVS Symp. 1996
ZnO(Ga)	90	2.7	13	18	230	Imaeda, K.et al 43rd AVS Symp. 1996
$ZnSnO_3$	80	45	1	20	310	Minami, T.et al, JVST A 13(3) 1995
Zn_2SnO_4	92	570	0.058	19.0	620	Wu, X.et al, JVST A 15(3),1997
$Zn_2In_2O_5$	95	2.9	6.0	30	400	Minami, T.et al, Thin Solid Films 290-291, 1996
$Zn_3In_2O_6$	80	3.8	3.4	46	1400	Phillips, J.et al Appl. Phys. Lett. 67(15) 1995
ITO	91	1-2	10	37	140	Heiz,b.,OIC Topical Meeting, 1998

EMERGING TRANSPARENT CONDUCTING OXIDES FOR ELECTRO-OPTICAL APPLICATIONS

CHARACTERISTICS OF EMERGING TCO MATERIALS

Material	Transmittance (%)	Resistivity ($x10^{-4}\Omega cm$)	Carrier Concentration ($x10^{20}cm^{-3}$)	Mobility ($cm^2/V^{-1}s^{-1}$)	Film Thickness (nm)	References
$MgIn_2O_4$	85	20	1.8	15		Minami, T. et al, Thin Solid Films 270,1995
$MgIn_2O_4$-$Zn_2In_2O_5$	82	10	3	2	400	Minami, T.et al ICMC TF 1995
In_2O_3 : Ga	85	5.8	5	20	400	Minami, T.et al JVST A 15(3)1997
$GaInO_3$ (Sn,Ge)	90	29	4	10	1000	Phillips, J.et al Appl. Phys. Lett. 65(1) 1994
$(GaIn)_2O_3$	90	10	3	20	100	Minami, T.et al JVST A 15(3)1997
ITO	91	1-2	10	37	140	Heiz,b.,OIC Topical Meeting, 1998

SOCIETY OF VACUUM COATERS

SHORT COURSE

ON

Deposition and Properties of ITO and Other Transparent Conductive Coatings

BY

Clark I. Bright
Delta V Technologies, Inc.

Appendix C

DEPOSITION AND PROPERTIES OF ITO AND OTHER TRANSPARENT CONDUCTIVE COATINGS (TCC)

OUTLINE (PART I)

I. FUNDAMENTALS OF CONDUCTIVITY AND THIN FILM OPTICS p. 5

II. TCC FUNCTION AND PERFORMANCE IN APPLICATIONS p. 41

III. MAJOR DEPOSITION METHODS FOR TCC p. 44

IV. IMPORTANT PROCESS PARAMETER FOR TRANSPARENT CONDUCTIVE OXIDES (TCO) p. 65

V. DEVELOPING A TCO DEPOSITION PROCESS p. 67

VI. TCC PROCESS EXAMPLES AND ASSOCIATED COATING PROPERTIES p. 84

DEPOSITION AND PROPERTIES OF ITO AND OTHER TRANSPARENT CONDUCTIVE COATINGS (TCC)

OUTLINE (PART II)

VII. STRATEGY FOR DEVELOPING A TCC TO MEET SPECIFIC APPLICATION REQUIREMENTS p.103

VIII. APPLICATION EXAMPLES

IX. SPECIFYING AND SELECTING COMMERCIALLY AVAILABLE TCC p.105

X. ADVANCED TOPICS p. 111

XI. QUESTIONS AND ANSWERS

HISTORY OF TRANSPARENT CONDUCTIVE COATINGS

- FIRST TRANSPARENT CONDUCTIVE COATING (TCC) WAS CADMIUM OXIDE USED IN PHOTOVOLTAIC CELLS IN 1907

- IN THE 1940's TIN OXIDE WAS DEPOSITED ON GLASS BY PYROLYSIS AND CHEMICAL VAPOR DEPOSITION

- IN THE 1950's THIN METALS, e.g. GOLD, WERE VACUUM EVAPORATED ON GLASS AND PLASTICS

- IN THE 1970's INDIUM OXIDE AND TIN DOPED INDIUM OXIDE (ITO) WERE MADE BY EVAPORATION AND DIODE SPUTTERING

- IN THE 1980's MAGNETRON SPUTTERING MADE IT POSSIBLE TO DEPOSIT ITO ON GLASS AND PLASTICS AT LOW TEMPERATURES WITH GOOD PERFORMANCE

- TODAY MAJOR TCC USED IN DISPLAYS AND OTHER APPLICATIONS IS ITO

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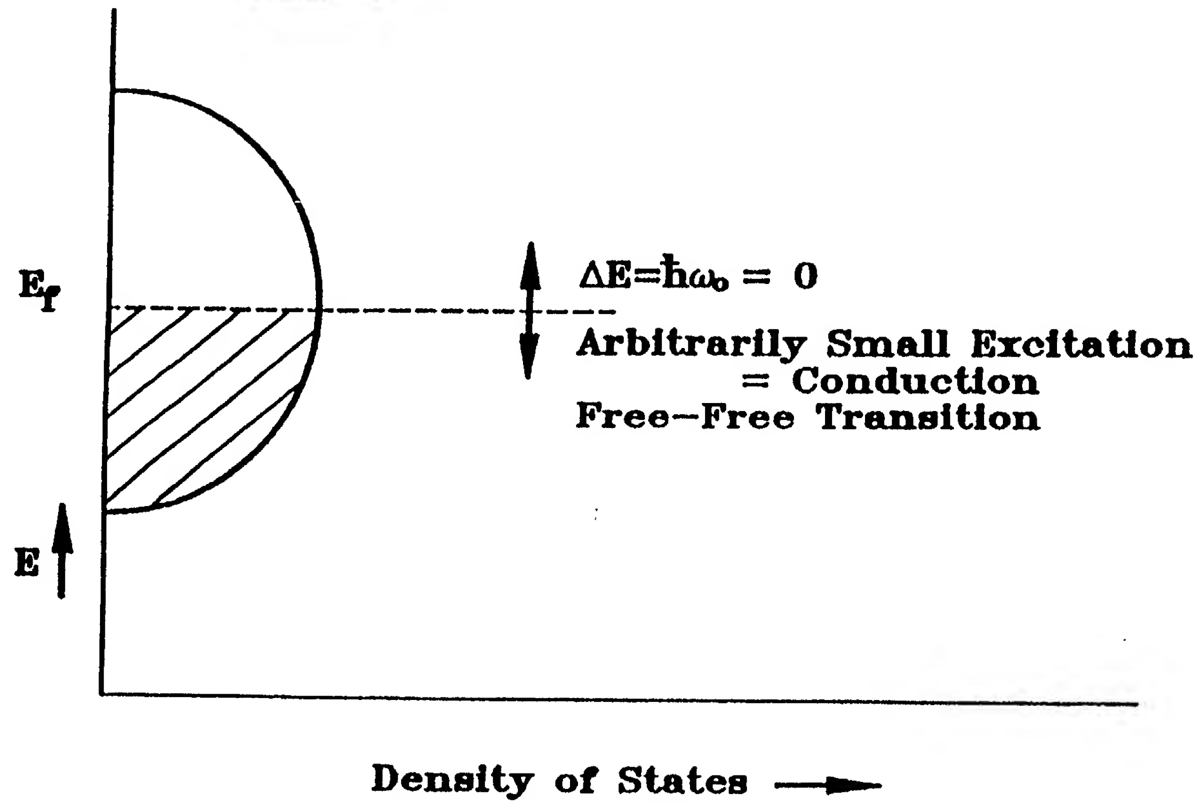
PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

METAL BAND STRUCTURE

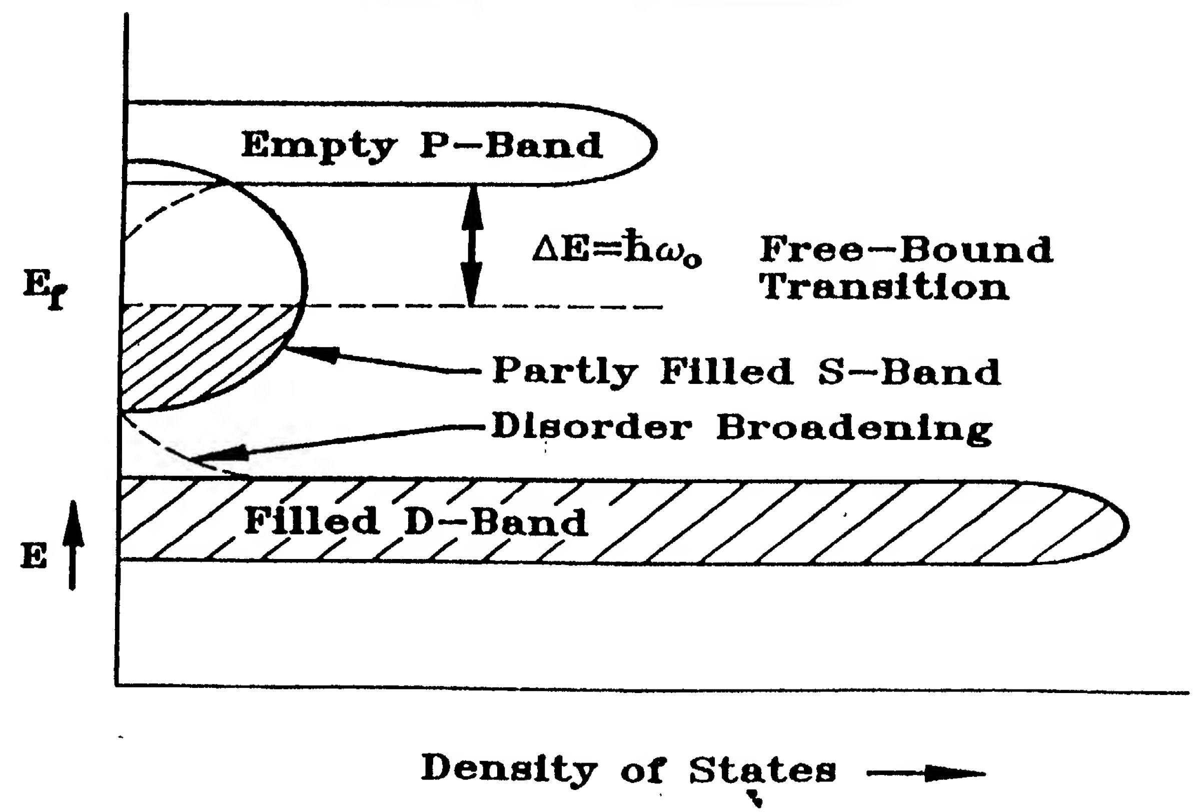
S–BAND FREE ELECTRONS



PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

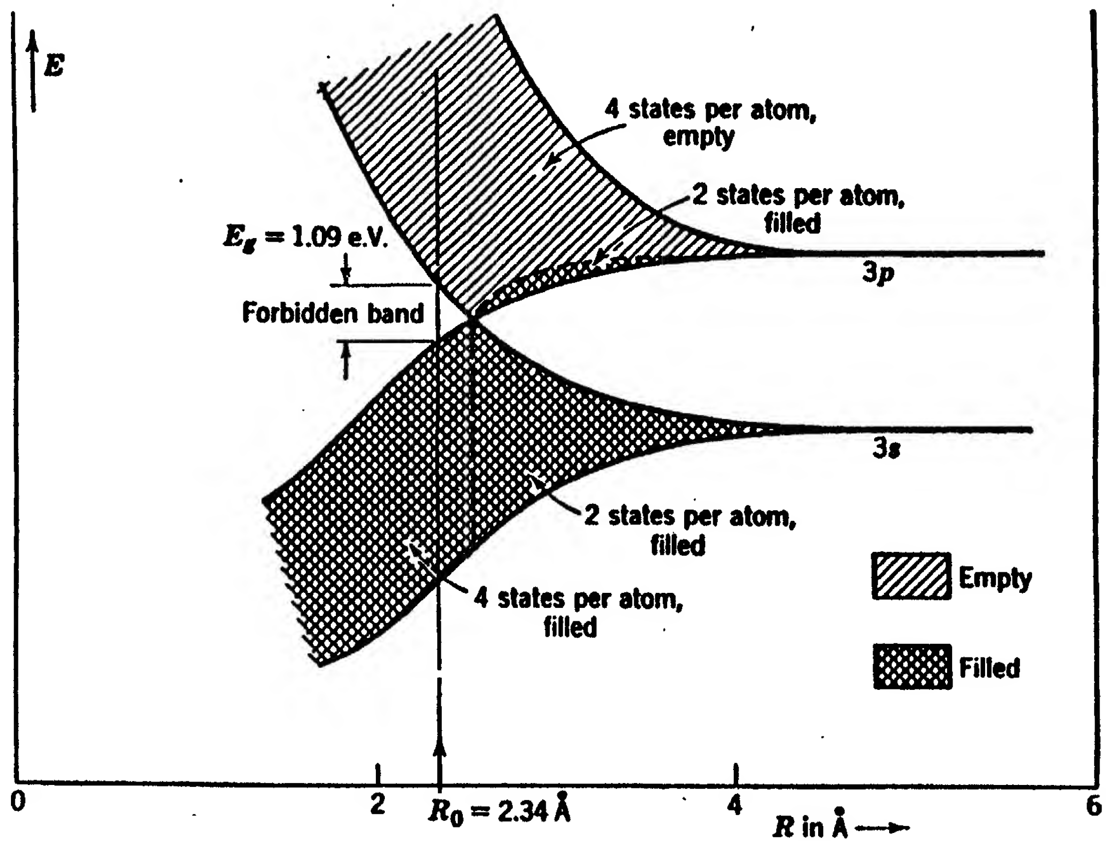
METAL BAND STRUCTURE

REAL S-BAND METAL



PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

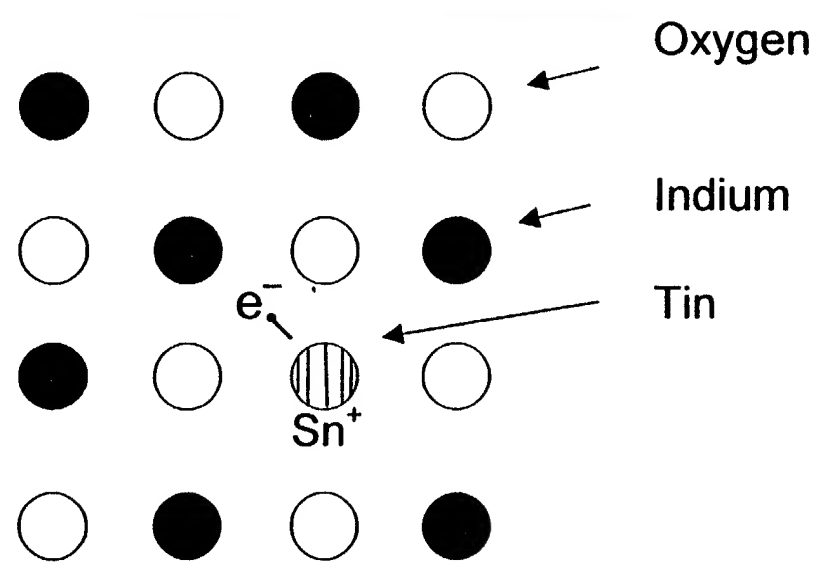
SEMICONDUCTOR BAND STRUCTURE



Energy Bands of Silicon as a Function of Nearest-Neighbor Distance (R)
(From R. L. Sproull, Modern Physics, Wiley, 1956)

PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

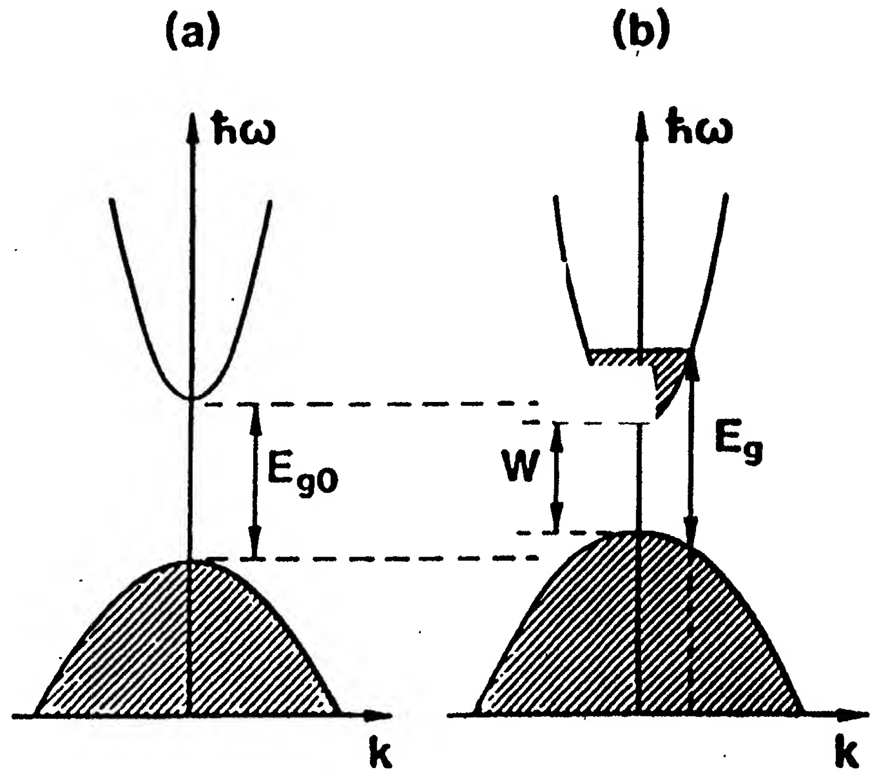
CRYSTAL STRUCTURE



Simplified Crystal Structure and Doping Model for Indium Tin Oxide
(C.G. Granqvist, Spectrally Selective Surfaces for Heating and Cooling Applications, TT 1 SPIE, 1989)

PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

BAND STRUCTURE



Assumed Band Structure for Undoped (a) and Tin Doped (b) Indium Oxide
Shaded Areas Indicate Occupied States
(C. G. Granqvist, Spectrally Selective Surfaces for Heating and Cooling Applications, TT 1, SPIE, 1989)

PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

CONDUCTIVITY

- METALS: $\sigma(\omega) = j\omega\varepsilon(\omega)$

  AND FOR DC ($\omega = 0$) $\sigma = N\,e\,\mu = \dfrac{N\,e^2\,\tau}{m} = \omega_p^{\,2}\,\tau$

  WHERE
  N = NUMBER DENSITY OF ELECTRONS
  e = ELECTRONIC CHARGE
  μ = ELECTRON MOBILITY
  τ = SCATTERING TIME
  m = ELECTRON MASS
  ω_p = PLASMA FREQUENCY
  ω = ANGULAR FREQUENCY OF RADIATION

- SEMICONDUCTORS:

  THE SAME FUNCTIONAL RELATIONS ARE DERIVED FOR BOTH ELECTRONS AND HOLES. TCO ARE HIGHLY DEGENERATE n-TYPE SEMICONDUCTORS SO EXPRESSION FOR σ IS THE SAME AS FOR METALS.

PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

CONDUCTIVITY

- CONDUCTIVITY OF A METAL DEPENDS ONLY ON THE NUMBER (DENSITY) OF ELECTRONS AND THEIR MOBILITY (SCATTERING TIME)
- FOR A SEMICONDUCTOR, THE CONDUCTION ELECTRONS ARE CREATED BY DOPING OR BY LACK OF STOICHIOMETRY
- FOR A TRANSPARENT CONDUCTING OXIDE (TCO), ITO et al, THE CONDUCTION ELECTRONS ARE CREATED PRIMARILY BY OXYGEN DEFICIENCIES (VACANCIES)
- THESE VACANCIES ARE CHARGE DEFECTS IN THE TCO LATTICE WHICH SCATTER ELECTRONS
- ELECTRON MOBILITY OR SCATTERING TIME DEPENDS ON THE DOPING LEVEL AS WELL AS THE TCO CRYSTALLOGRAPHIC ORDER

PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

<u>CONDUCTIVITY</u>

- FOR A GIVEN TCO DEPOSITION PROCESS THERE IS A RESISTIVITY MINIMUM
- AT LOW DOPING LEVELS THE RESISTIVITY IS INCREASED BY LACK OF CONDUCTION ELECTRONS
- AT HIGH DOPING LEVELS THE RESISTIVITY IS INCREASED BY ELECTRON SCATTERING FROM OXYGEN VACANCIES
- THE MINIMUM RESISTIVITY OCCURS WHEN SCATTERING CAUSED BY DOPING IS COMPARABLE TO SCATTERING FROM ALL OTHER DEFECTS

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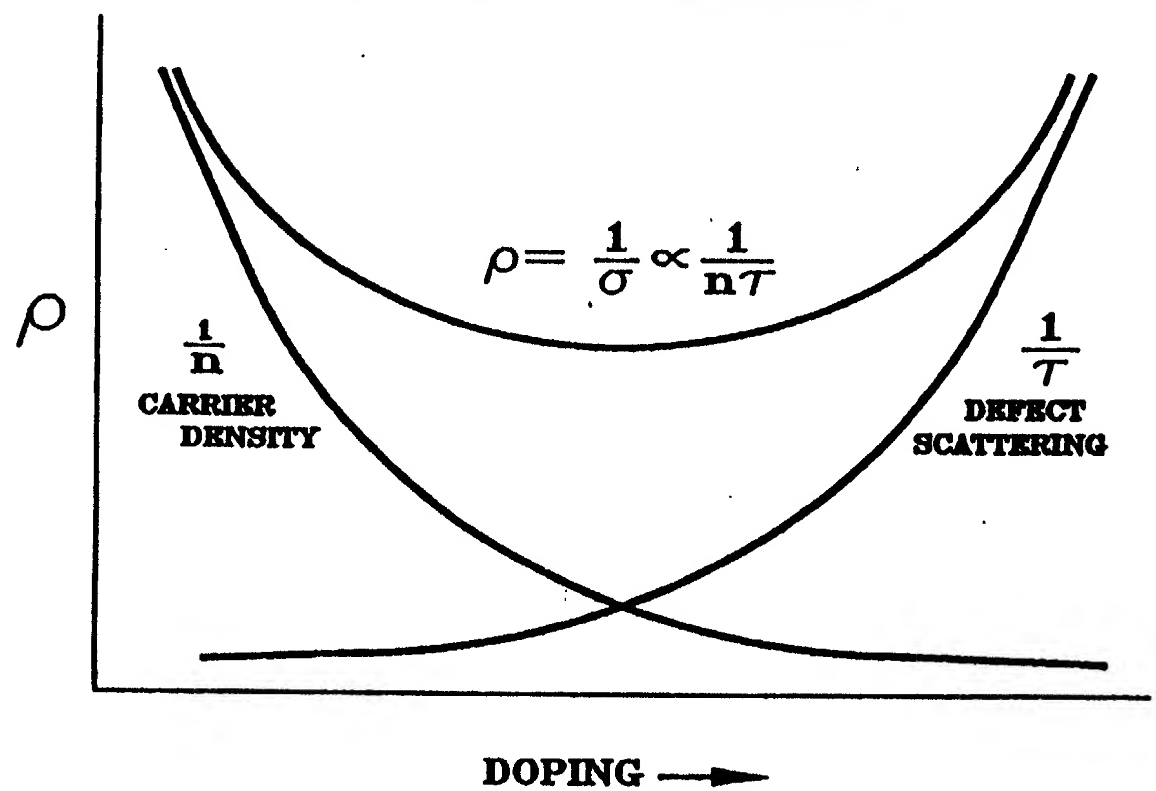
PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

RESISTIVITY vs DOPING



ORIGIN OF RESISTIVIETY WELL

PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

CARRIER ABSORPTION

- THE FREE CARRIERS NEEDED FOR CONDUCTION WILL ABSORB INCIDENT ELECTROMAGNETIC (EM) RADIATION

- ABSORPTION COEFFICIENT (α) VARIES WITH WAVELENGTH

$$\alpha = \frac{4 \pi k}{\lambda}$$

WHERE k IS THE EXTINCTION COEFFICIENT AND λ IS THE WAVELENGTH

- METALS AND SEMICONDUCTOR HAVE CHARACTERISTIC SPECTRAL OPTICAL PROPERTIES

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PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

DRUDE THEORY

- THE DIELECTRIC FUNCTION FOR CONDUCTION (FREE) ELECTRONS:

  $\varepsilon(\omega) = \varepsilon_1 - i\varepsilon_2 = n^2$ AND $n = \text{n} - \text{ik}$ THEN $\varepsilon_1 = \text{n}^2 - \text{k}^2$ AND $\varepsilon_2 = 2\text{nk}$

  AND $\varepsilon_1 = 0$ WHEN $\omega = \omega_p$ AND $\omega_p^2 = \dfrac{\text{N e}^2}{\varepsilon_0 \text{m}}$

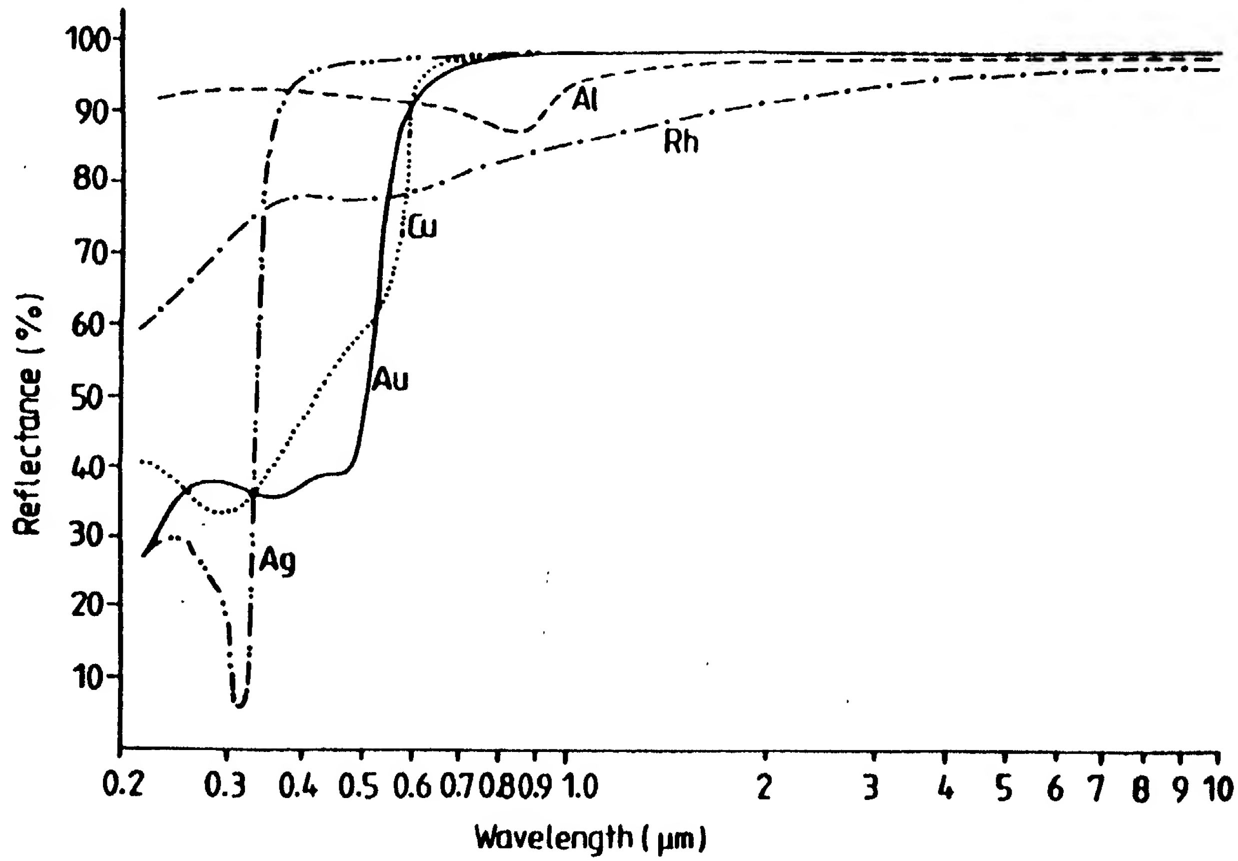
WHERE
N = NUMBER DENSITY OF ELECTRONS
e = ELECTRONIC CHARGE
τ = SCATTERING TIME
m = ELECTRON MASS
ω_p = PLASMA FREQUENCY
ω = ANGULAR FREQUENCY OF RADIATION

- METAL NITRIDES:

  $\varepsilon(\omega) = \varepsilon_1(\infty) - (\omega_p^2 / \omega^2 + i\omega/\tau)$ AND $\omega_p^2 = \dfrac{\text{N e}^2}{\varepsilon_0 \text{ m}^*}$

PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

OPTICS OF METALLIC THIN FILMS



Change in Reflectance at Plasma Wavelength for Simple Metals (Au, Ag, Cu)
(From G. Hass, J. Opt. Soc. Am. 45, 945-52, 1955)

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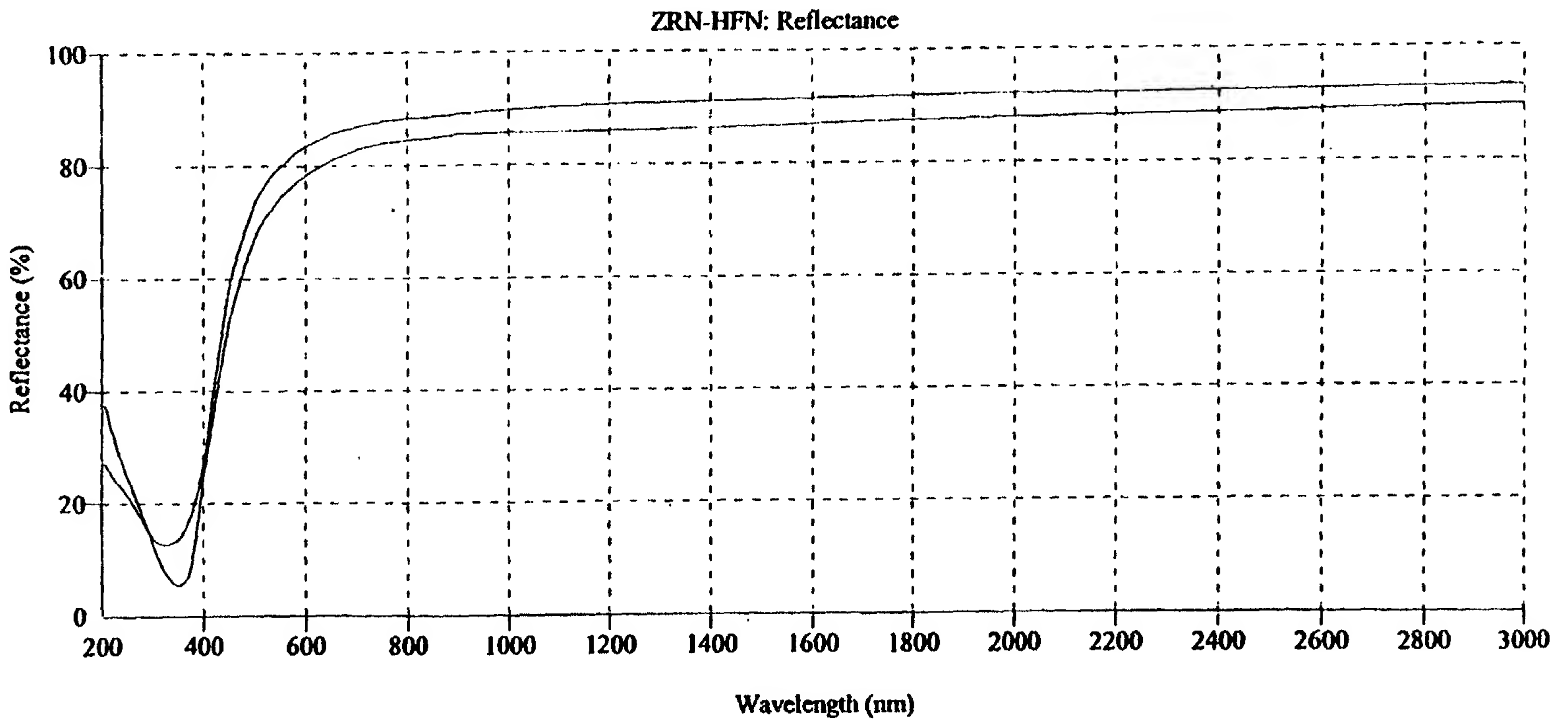
PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

OPTICS OF METALLIC NITRIDE THIN FILMS



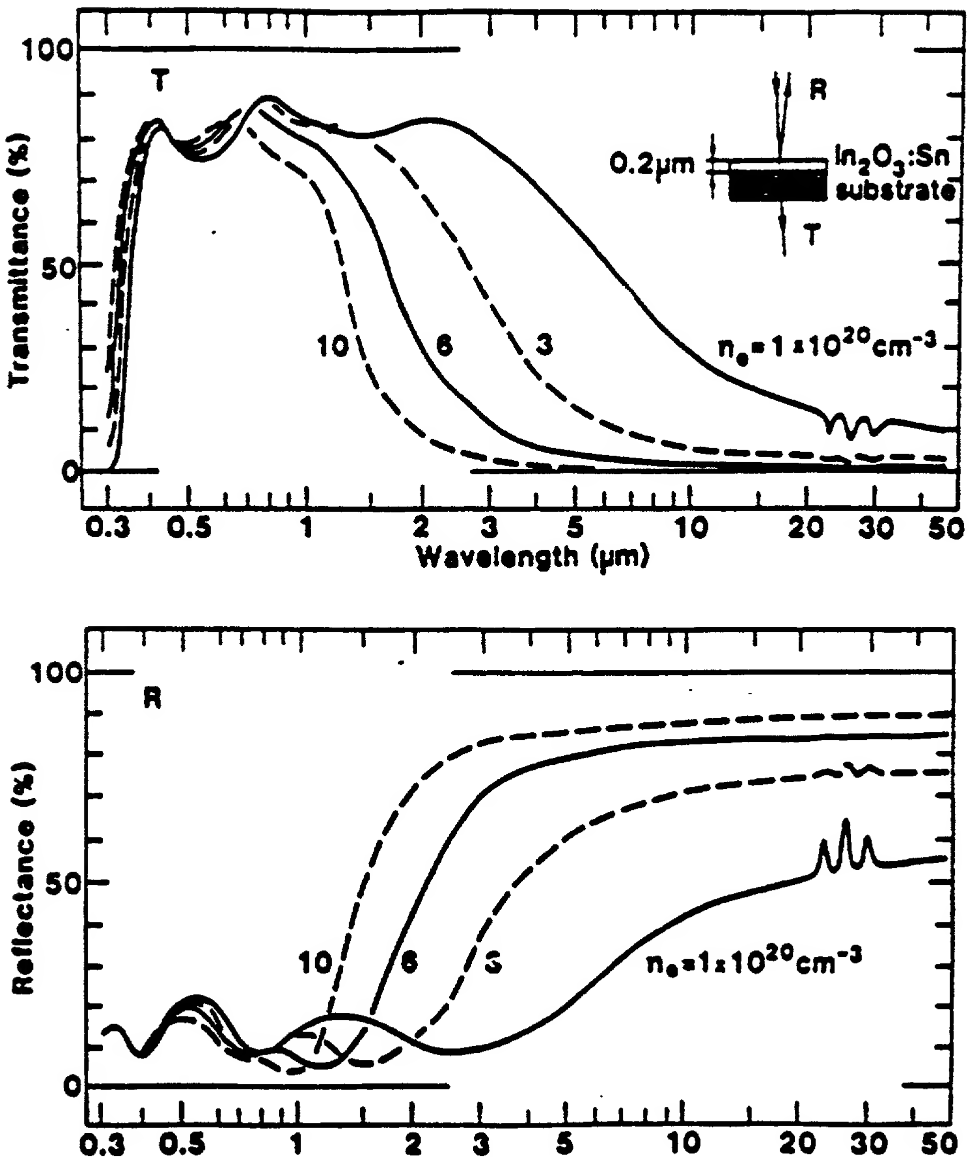
Change in Reflectance at Plasma Wavelength for HfN, ZrN

HfN – lower trace, ZrN – upper trace

(Calculated from optical constants in E.D. Palik, Ed. Handbook of Optical Constants of Solids III)

PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

CONDUCTIVITY



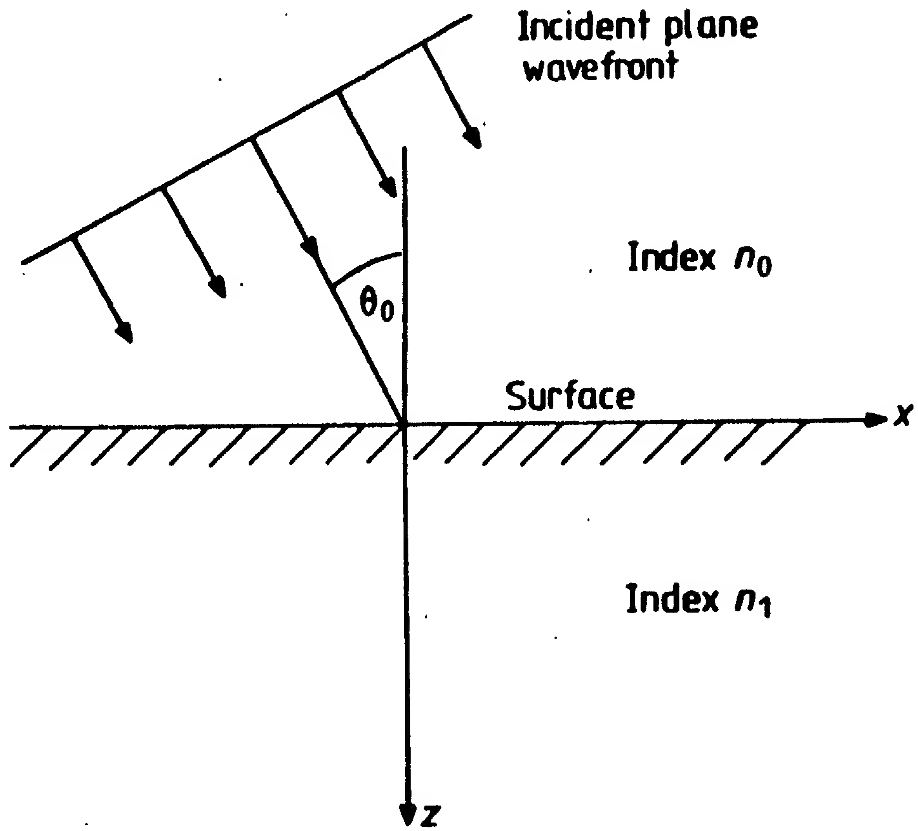
Spectral Properties of ITO as a Function of Carrier Density (Ne)

(From, J. App. Opt, 24, 12 15june 1985)

19

PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

THIN FILM OPTICS



Plane Wave Incident on a Single Surface
(From Thin Film Optical Filters, H. A. Macleod, Macmillan, 1968)

PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

THIN FILM OPTICS

REFLECTANCE OF SINGLE SURFACE

$$R = \left\{\frac{n_{MEDIUM} - n_{FILM}}{n_{MEDIUM} + n_{FILM}}\right\}^2$$

EX: FOR $n_{FILM} = 2.0$ and $n_{MEDIUM} = 1.0$ (AIR)

$$R = \left\{\frac{1 - 2}{1 + 2}\right\}^2 = 0.11111 = 11.1\% \text{ (PER SURFACE)}$$

EX: FOR $n_{FILM} = 1.51$ and $n_{MEDIUM} = 1.0$

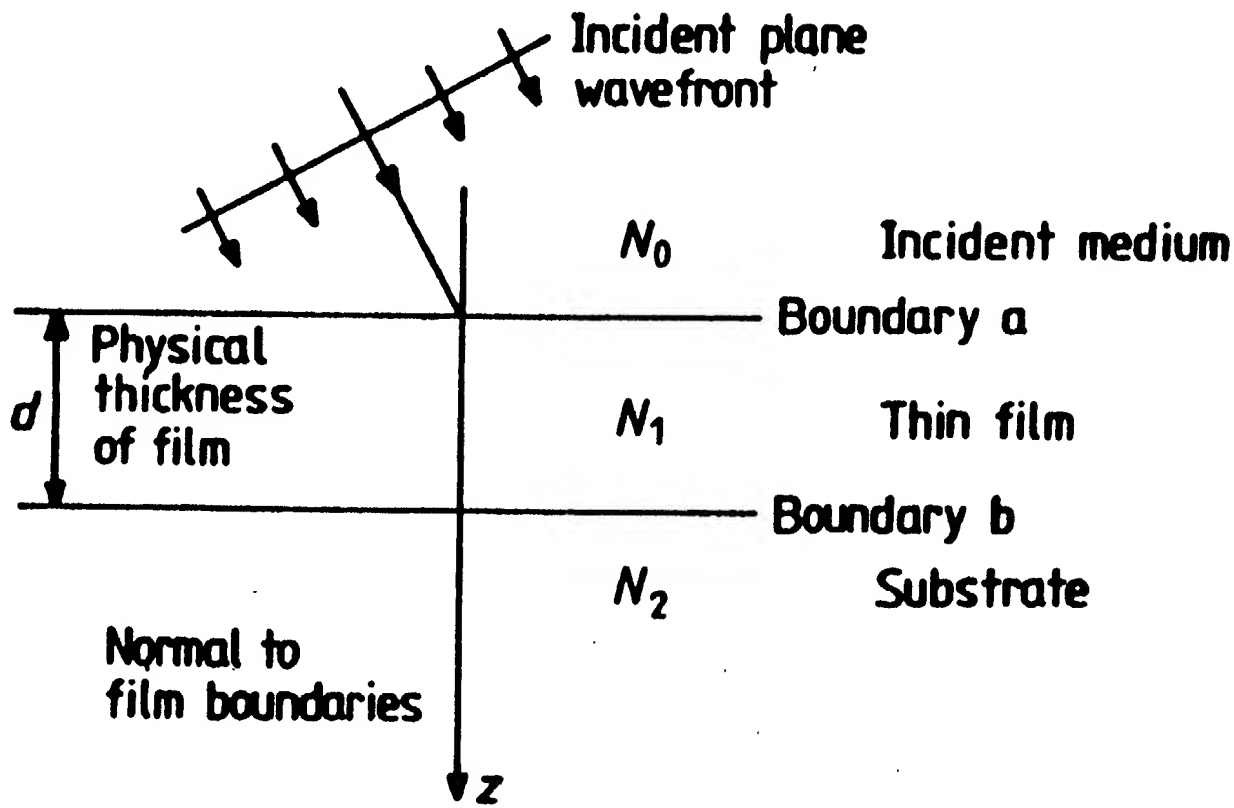
$$R = \left\{\frac{1 - 1.51}{1 + 1.51}\right\}^2 = 0.0413 = 4.1\% \text{ (PER SURFACE)}$$

EX: FOR $n_{FILM} = 2.0$ and $n_{SUB} = 1.51$

$$R = \left\{\frac{n_{SUB} - n_{FILM}}{n_{SUB} + n_{FILM}}\right\}^2 = \left\{\frac{1.51 - 2.0}{1.51 + 2.0}\right\}^2 = 0.0195 = 1.95\%$$

PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

THIN FILM OPTICS



Plane Wave Incident on a Thin Film
(From Thin Film Optical Filters, H. A. Macleod, Macmillan, 1968)

PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

THIN FILMS OPTICS

- OPTICAL THICKNESS IS THE PRODUCT OF INDEX OF REFRACTIONS AND PHYSICAL THICKNESS = n x d (WAVES)

- QUARTERWAVE OPTICAL THICKNESS = n x d = $\frac{\lambda}{4}$

  EX: FOR n = 2 AND d = 100 NM

  $\lambda_{1/4}$ = 4 nd = 800 NM

- HALFWAVE OPTICAL THICKNESS = n x d = $\frac{\lambda}{2}$

  EX: FOR n = 2 AND d = 100 NM

  $\lambda_{1/2}$ = 2 nd = 400 NM

PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

THIN FILM OPTICS

- SINGLE LAYER ON A SUBSTRATE

$$R_M = \left\{\frac{n^2_{FILM} - n_O\, n_{SUB}}{n^2_{FILM} + n_O\, n_{SUB}}\right\}^2$$ WHERE n_O IS THE INCIDENT MEDIUM INDEX

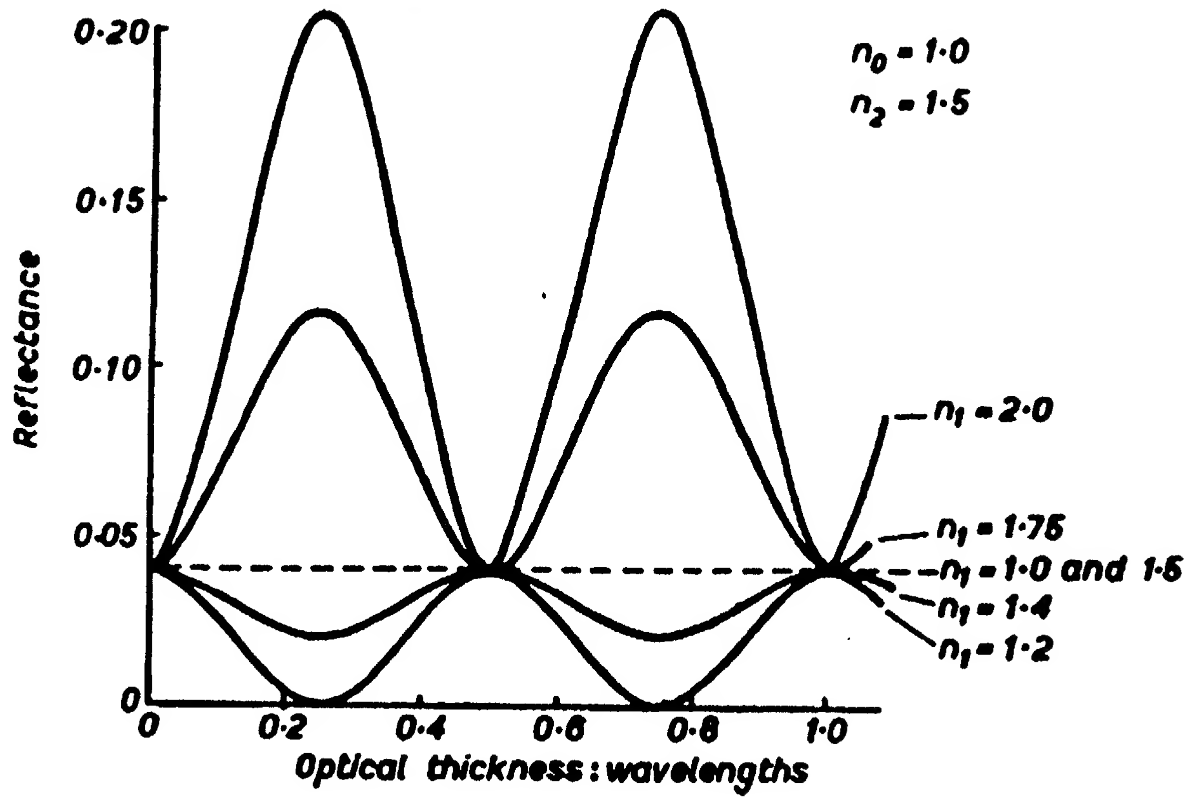
R_M IS EITHER A MAXIMUM OR A MINIMUM IF THE OPTICAL THICKNESS IS AN ODD MULTIPLE OF A QUARTERWAVE, e.g. $\frac{\lambda}{4}$, $\frac{3\lambda}{4}$, $\frac{5\lambda}{4}$, etc

EX: FOR $n_{FILM} = 2.0$, $n_{SUB} = 1.51$ AND $n_O = 1.0$

$$R_M = \left\{\frac{4 - 1.51}{4 + 1.51}\right\}^2 = 0.2042 = 20.42\%$$

PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

THIN FILM OPTICS



Variation of reflectance (at air side) with thickness for films of various refractive indices on a substrate of index 1.5

(From O.S. Heavens, Optical Properties of Thin Solid Films, Dover, 1985)

PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

THIN FILMS

SURFACE RESISTIVITY

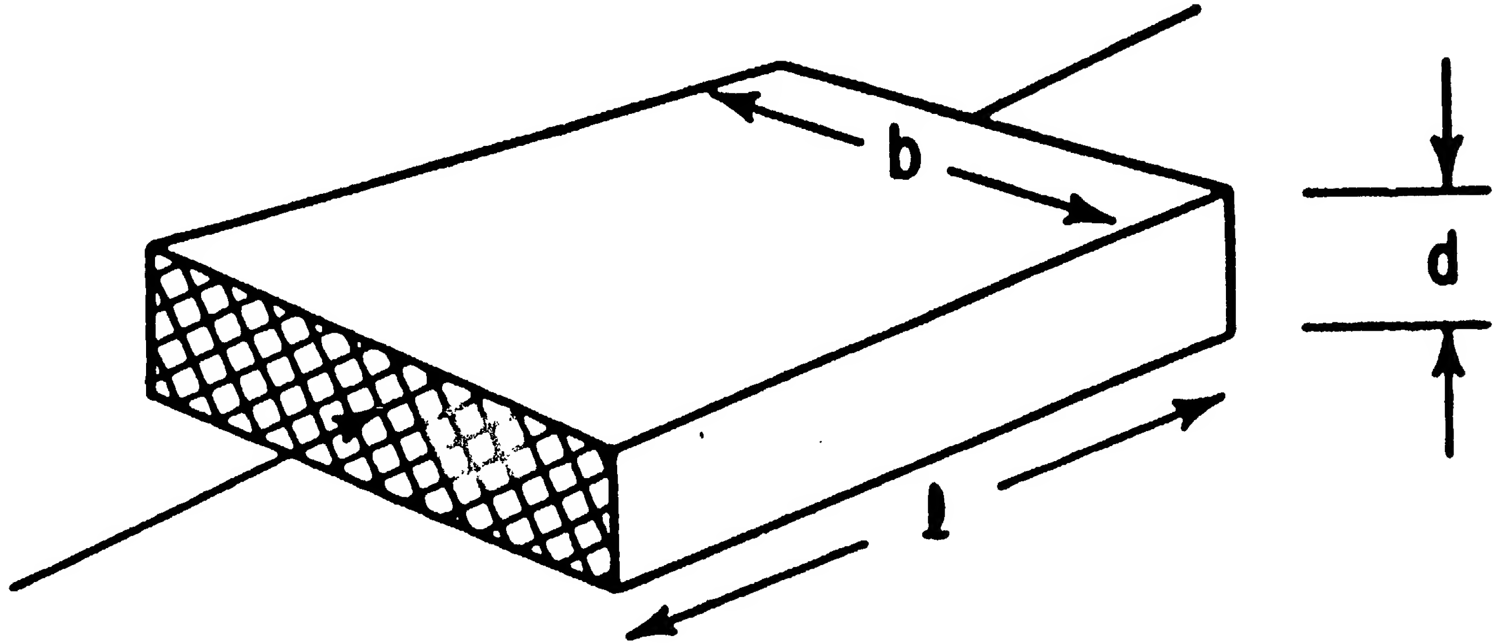
- CONDUCTIVITY IS RECIPROCAL OF VOLUME RESISTIVITY (ρ)

  $$\rho = \frac{1}{\sigma} \text{ OHM - CM}$$

- HOWEVER, VOLUME RESISTIVITY CAN BE MISLEADING BECAUSE THIN FILMS ARE OFTEN INHOMOGENEOUS, CONTAIN DEFECTS, CAN EXHIBIT SURFACE SCATTERING, AND FILM THICKNESS IS DIFFICULT TO MEASURE ACCURATELY

- THEREFORE SURFACE (SHEET) RESISTIVITY (r) IS USED

PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS



SURFACE RESISTIVITY

$$R = \frac{p \times \ell}{b \times d} \text{ OHMS}, \qquad R = p \times \frac{\ell}{d} = r \times \frac{\ell}{b} \text{ OHMS}$$

$$r = R \times \frac{b}{\ell} \text{ IN UNITS CALLED OHMS/SQUARE}$$

BECAUSE WHEN $\ell = b$, I.e., ON A SQUARE AREA, THE SURFACE RESISTIVITY EQUALS THE MEASURED RESISTANCE, $r = R$ (OHMS)

PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

THIN FILMS

SURFACE RESISTIVITY

- NOTE THAT THE MEASURED VALUE OF r IS INDEPENDENT OF THE SIZE OF THE SQUARE (AREA)
- IT IS ONLY DEPENDENT ON THE GEOMETRIC RATIO OF WIDTH TO LENGTH (b/l)
- THUS A SQUARE INCH OR A SQUARE METER OF COATING WILL HAVE THE SAME RESISTANCE

PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

THIN FILMS

SURFACE RESISTIVITY

- COMPARE THE THEORETICAL COATING THICKNESSES (BULK MATERIAL) OF TWO 10 OHMS/SQUARE THIN FILMS:

	ITO	GOLD
FOR	$\rho = 2 \times 10^{-4}$ OHM-CM	$\rho = 2.4 \times 10^{-6}$ OHM-CM
	$r = \frac{\rho}{d}$ = 10 OHMS/SQUARE	$r = \frac{\rho}{d}$ = 10 OHMS/SQAURE
	$d = \frac{\rho}{r} = 2 \times 10^{-5}$ CM	$d = \frac{\rho}{r} = 2.4 \times 10^{-7}$ CM
	d = 200 NM	d = 2.4 NM

- THUS FOR THE SAME OHMS/SQUARE, SEMICONDUCTOR TCC ~ 100X THICKER THAN METALLIC TCC

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PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

OPTICS

- SPECTRAL VALUES

TRANSMITTANCE IS $T(\lambda)$, REFLECTANCE $R(\lambda)$, ABSORPTANCE $A(\lambda)$

$T(\lambda) + R(\lambda) + A(\lambda) = 1$

- INTEGRATED VALUES:

AVERAGE - e.g. T AVERAGE = $$\int_{\lambda = 400NM}^{\lambda = 700NM} \frac{T(\lambda)\, d\lambda}{M\, d\lambda} = \sum_{\lambda = 400NM}^{\lambda = 700NM} \frac{T(\lambda)\, \Delta\lambda}{M\, \Delta\lambda}$$

WHERE M IS NUMBER OF WAVELENGTHS (INTERNALS)

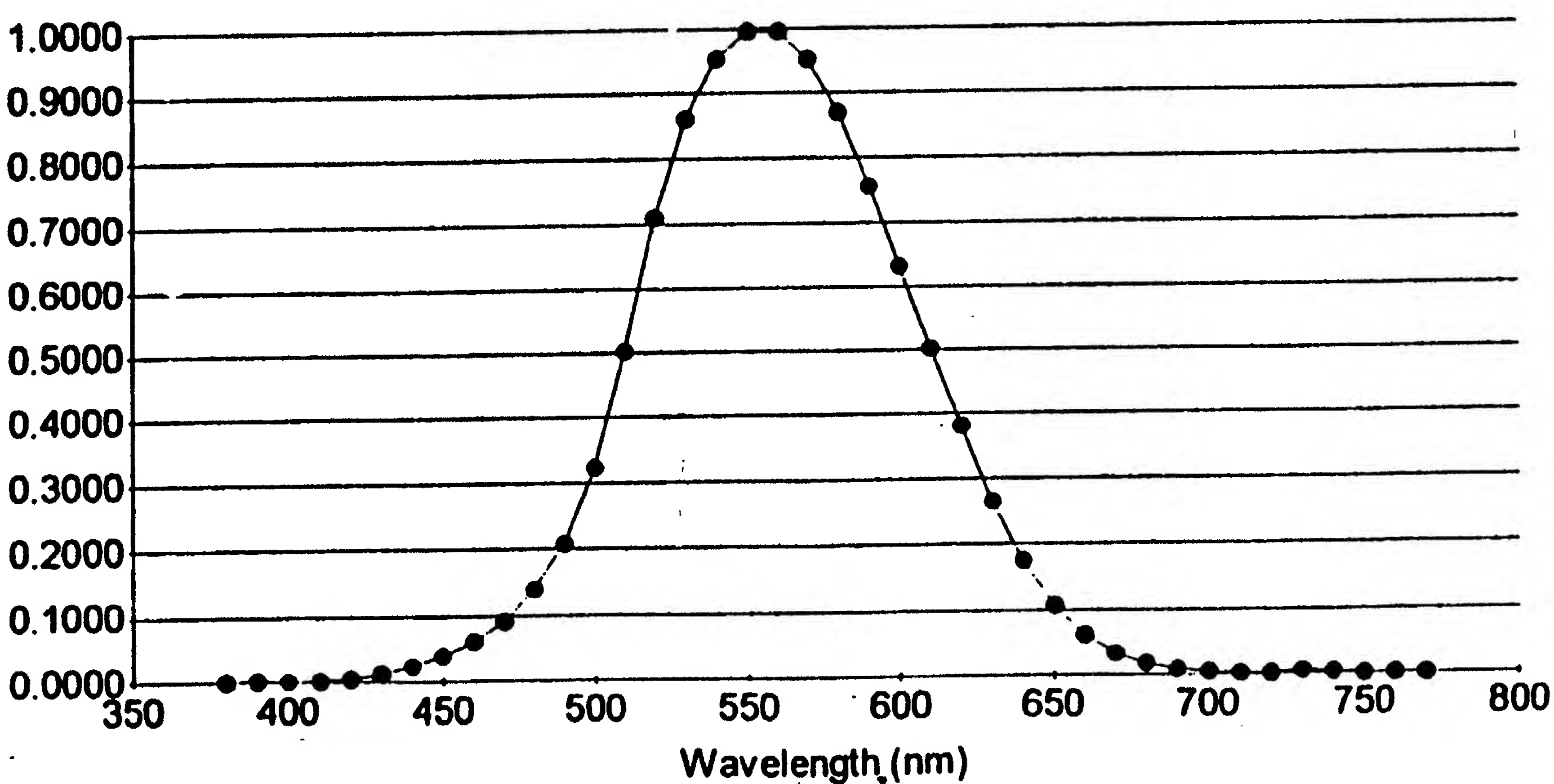
EYE WEIGHTED - LUMINOUS T = $$\int_{\lambda = 380NM}^{\lambda = 780NM} \frac{T(\lambda)K(\lambda)P(\lambda)d(\lambda)}{P(\lambda)K(\lambda)d(\lambda)} = \sum_{\lambda = 380NM}^{\lambda = 780NM} \frac{T(\lambda)K(\lambda)P(\lambda)\Delta(\lambda)}{P(\lambda)K(\lambda)\Delta(\lambda)}$$

WHERE $P(\lambda)$ IS AVERAGE DAYLIGHT AND $K(\lambda)$ IS RELATIVE SENSITIVITY OF PHOTOPIC ADAPTED EYE

"VISIBLE" - NOT DEFINED GENERALLY, OFTEN MEANS LUMINOUS

PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

OPTICS



PHYSICS FUNDMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

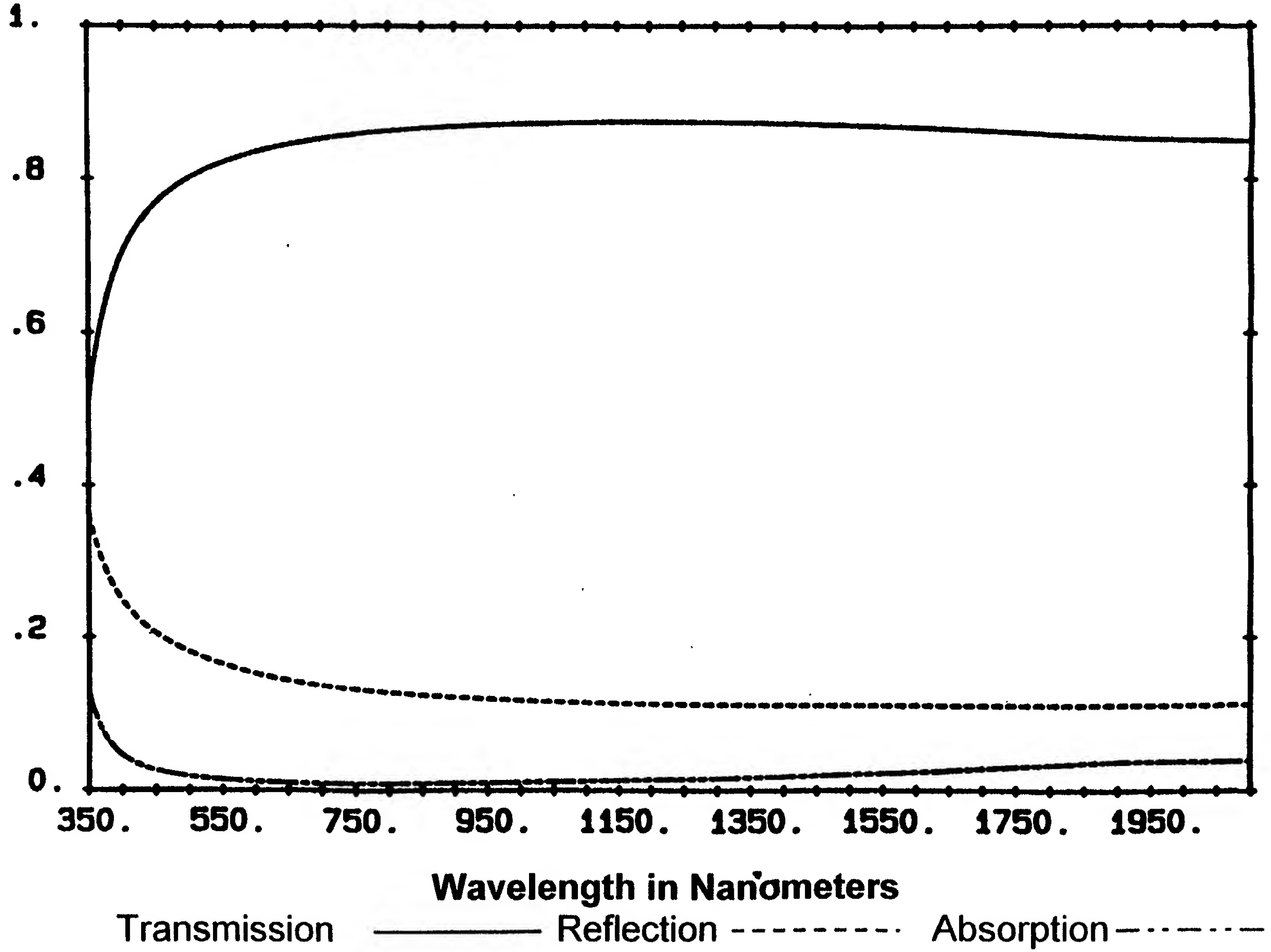
COLOR

Color	1ST Order t(Å)	2nd Order t(Å)	3rd Order t(Å)	4th Order t(Å)
Gray	75			
Tan	230			
Brown	380			
Blue	620			
Violet	770	2100	3600	5000
Blue	1150	2300	3800	5300
Green	1400	2500	4000	5550
Yellow	1600	2850	4300	5800
Orange	1750	3100	4600	6050
Red	1900	3350	4800	6300

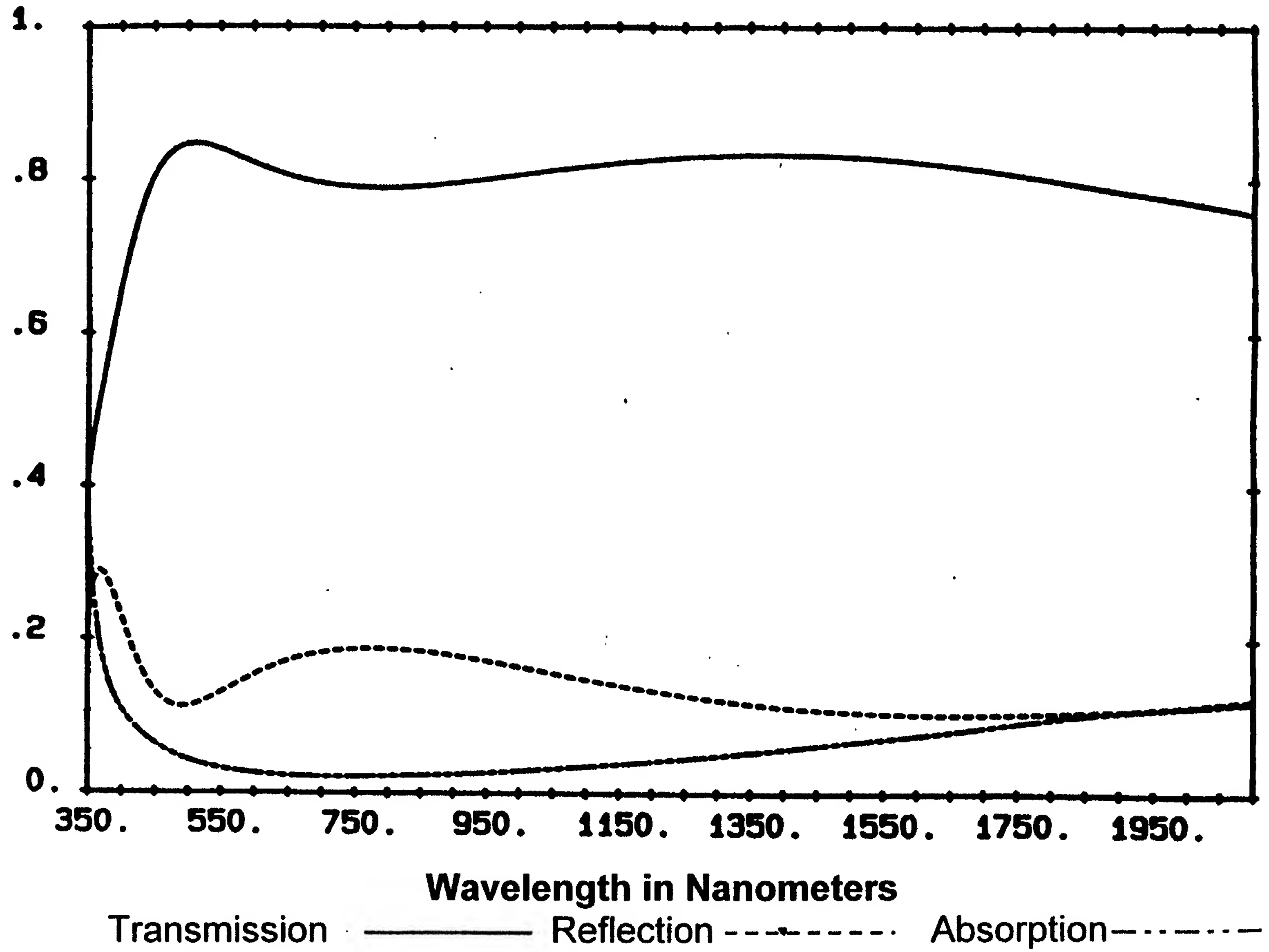
[a] $n = 2.00$.

Colors of TCO Thin Films When Viewed in Reflected White Light.
(From J.L. Vossen, Physics of Thin Films, Vol. 9, Academic Press, 1997)

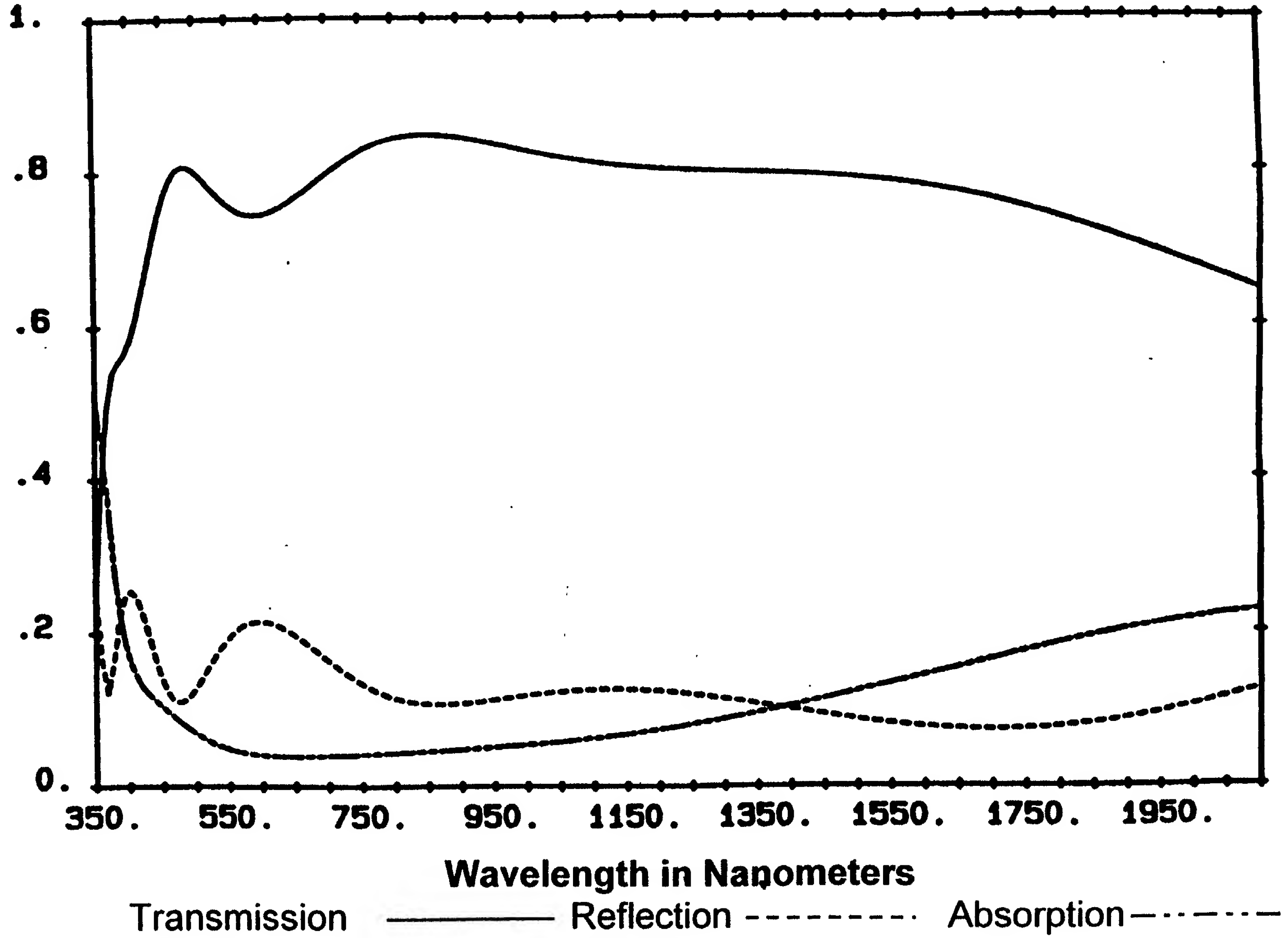
ITO 200 OHMS/SQUARE



ITO 60 OHMS/SQUARE

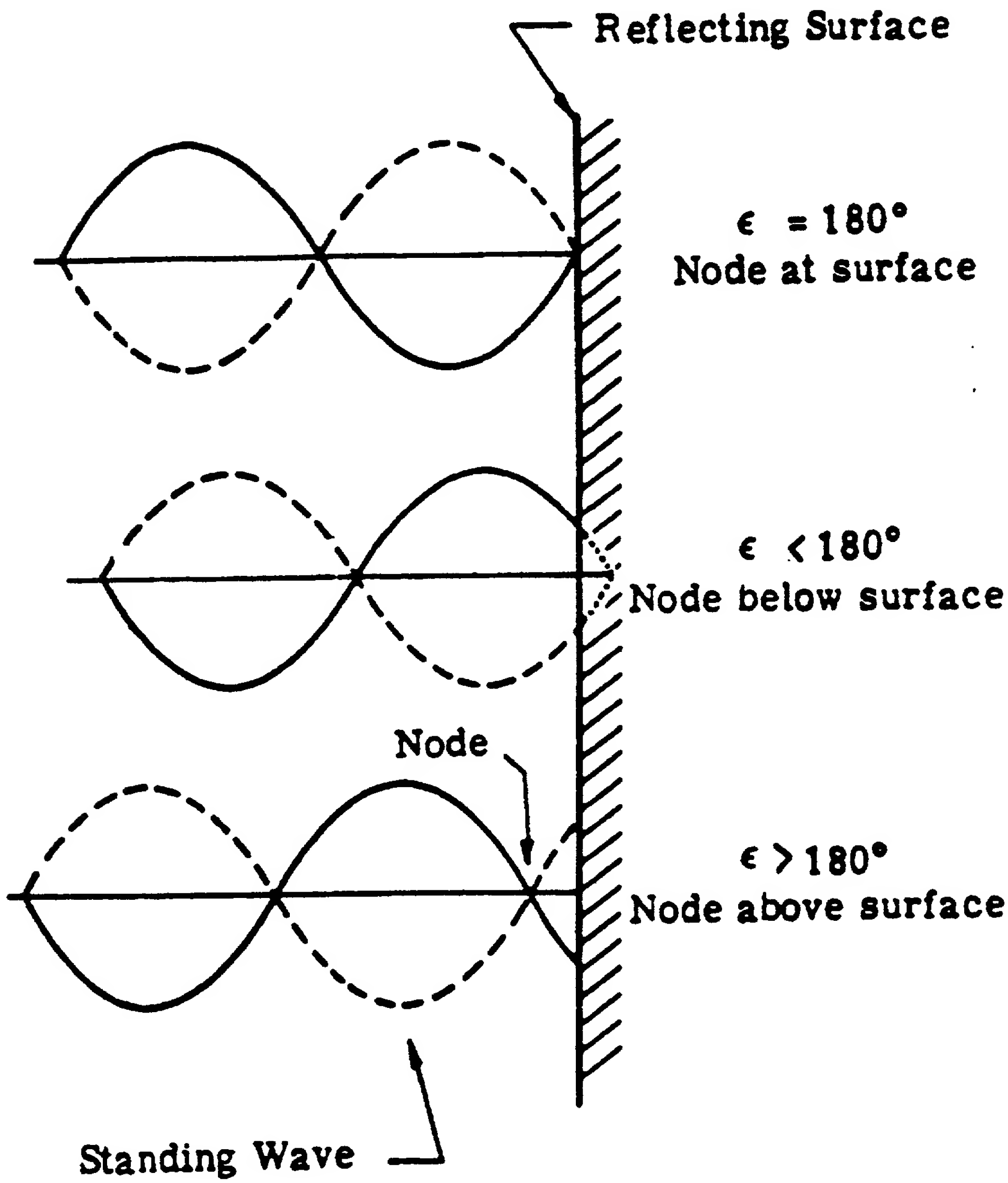


ITO 30 OHMS/SQUARE



PHYSICS FUNDAMENTAL OF TRANSPARENT CONDUCTIVE COATINGS

Thin Film Optics

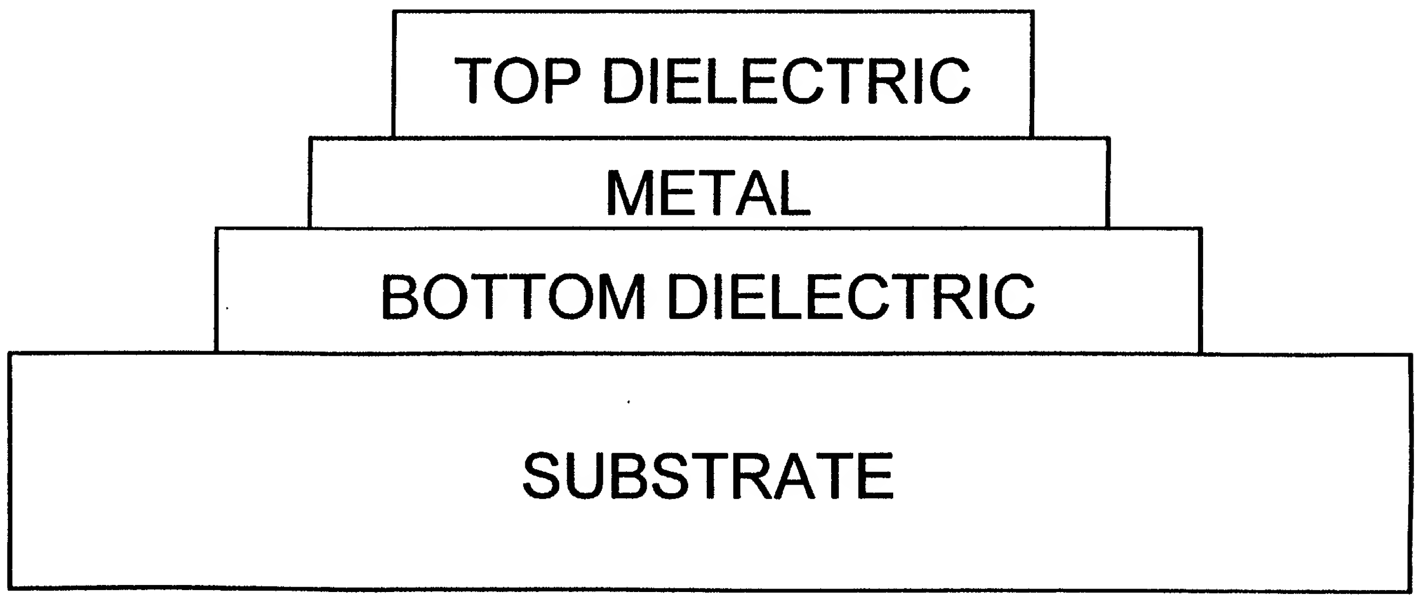


Phase Shift upon Reflection and Standing Wave

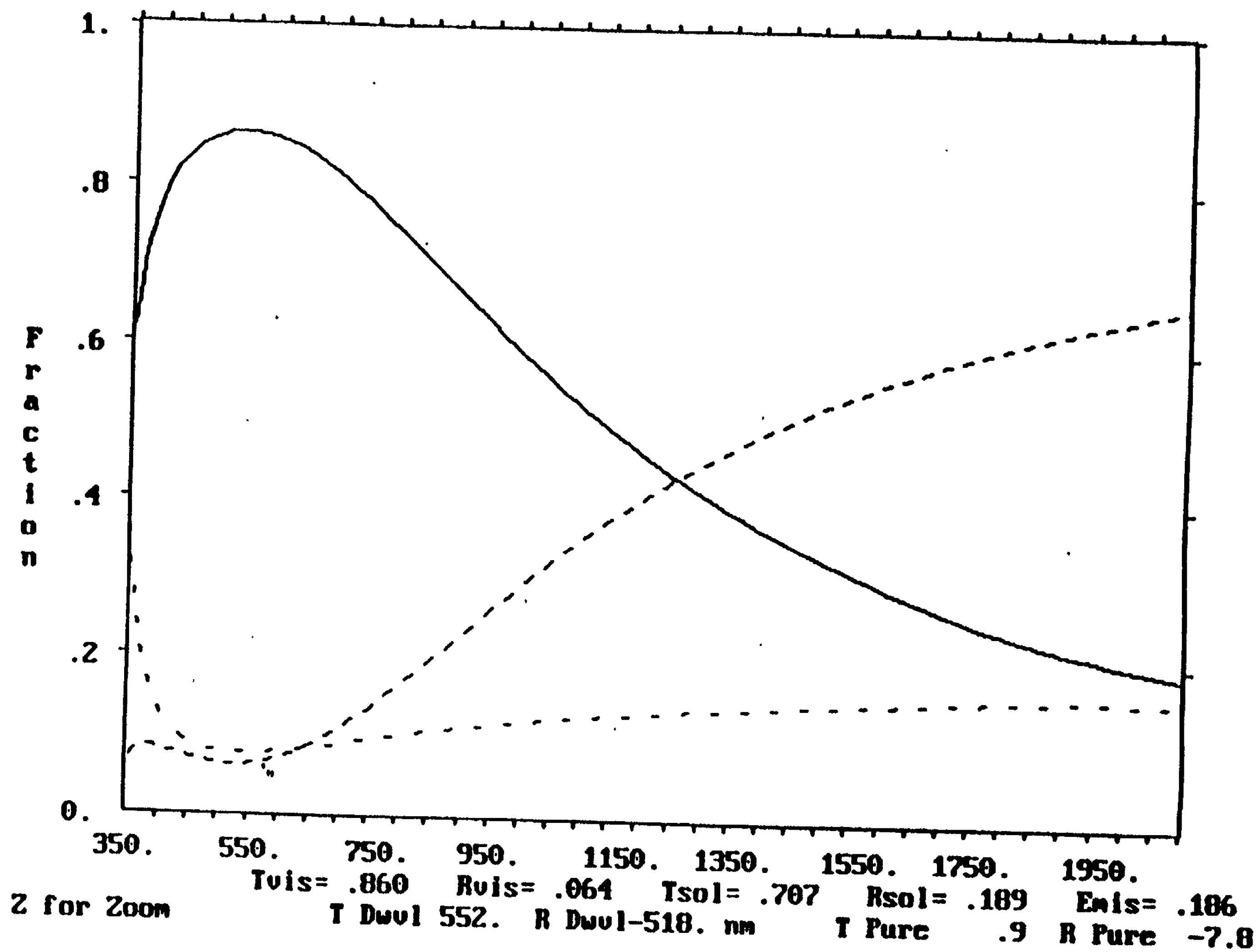
(From Mil. Std. Handbook, Optical Design, Mil – Hdbk – 141, 1962)

PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

<u>THIN FILM OPTICS</u>



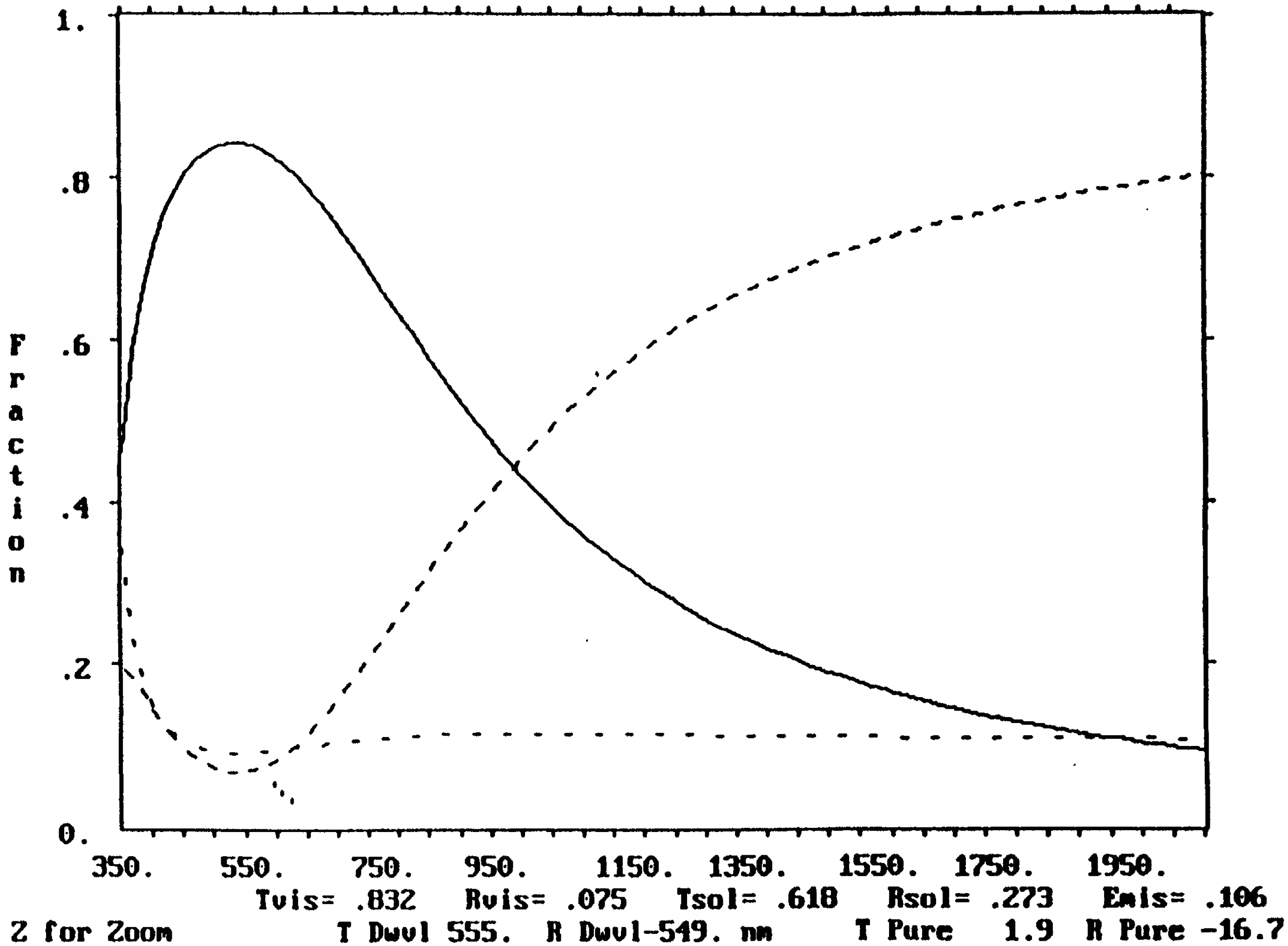
OPTICALLY ENHANCED METAL



Metal Oxide – Silver – Metal Oxide Coating on PET, 20 Ohms/Square

Transmittance – upper trace, Reflectance – middle trace, Aborptance – lower trace

OPTICALLY ENHANCED METAL



Metal Oxide – Silver – Metal Oxide Coating on PET, 10 Ohms/Square

Transmittance – upper trace, Reflectance – middle trace, Aborptance – lower trace

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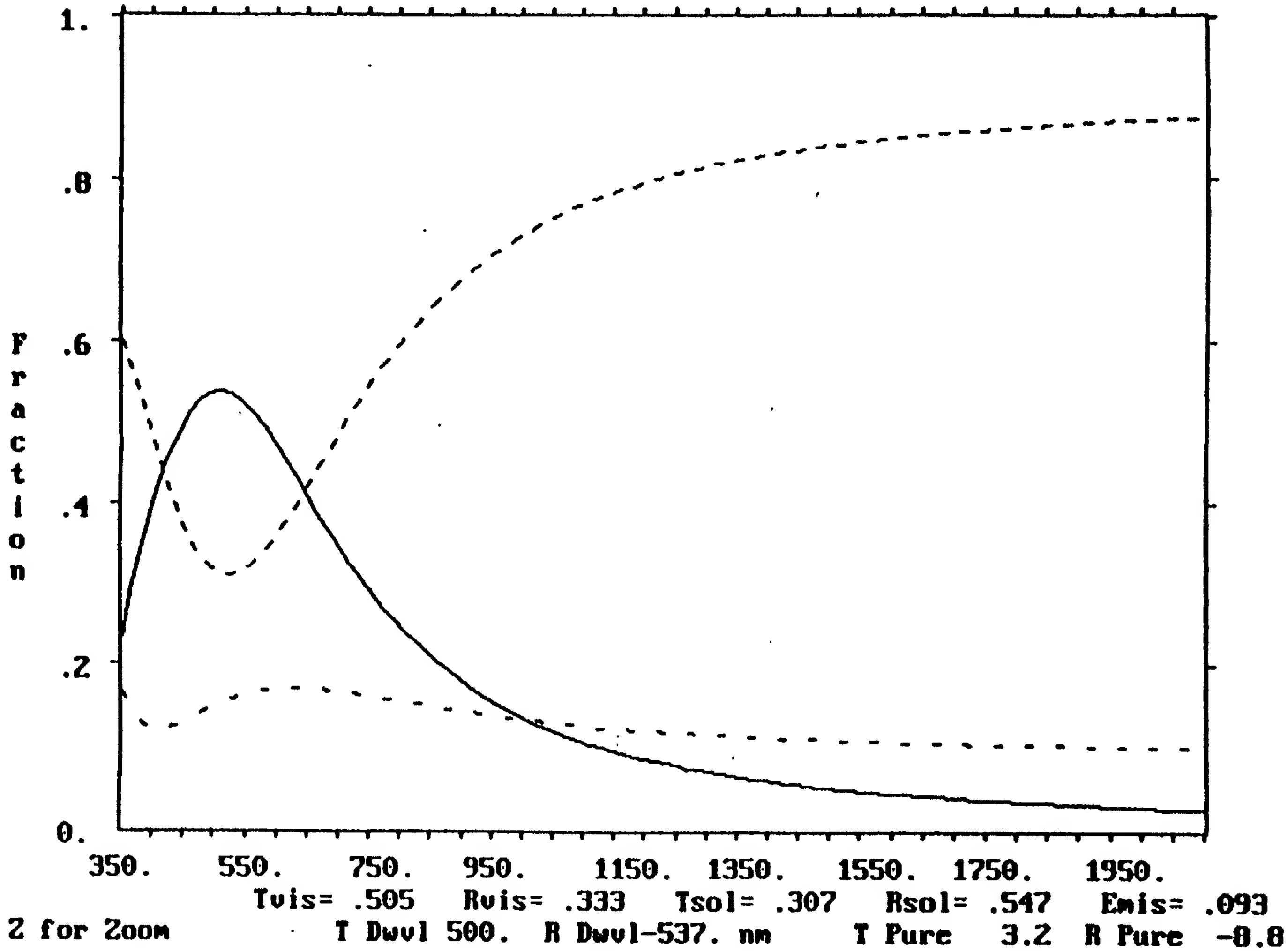
OPTICALLY ENHANCED METAL



Metal Oxide – Silver – Metal Oxide Coating on PET, 5 Ohms/Square

Transmittance – upper trace, Reflectance – middle trace, Aborptance – lower trace

PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

OPTICAL AND ELECTRICAL PERFORMANCE

- A COMPROMISE BETWEEN HIGH OPTICAL TRANSMITTANCE AND HIGH CONDUCTIVITY (LOW RESISTIVITY) IS ALWAYS REQUIRED
- OPTICAL TRANSMITTANCE IS FUNDAMENTALLY LIMITED BY ABSORPTION
- OPTICAL TRANSMITTANCE AND REFLECTANCE ARE WAVELENGTH DEPENDENT
- OPTICAL PERFORMANCE CAN BE GENERALIZED BY TYPE OF TCC (i.e. METAL OR SEMICONDUCTOR) AND WAVEBAND (UV, VIS, NEAR IR, MIDWAVE IR AND LONGWAVE IR)
- MANY FIGURES-OF-MERIT FOR TCC HAVE BEEN DEFINED BUT LIMITED USEFULNESS BECAUSE NEED TO BE APPLICATION SPECIFIC

SPECIFYING AND SELECTING TRANSPARENT CONDUCTIVE COATINGS

FUNCTION

TRANSPARENT ELECTRODE:

- REQUIREMENT IS TO APPLY AN ELECTRICAL FIELD
- THEREFORE, COMPROMISE IS FOR HIGH TRANSMITTANCE WITH LOW CONDUCTIVITY (HIGH RESISTIVITY)

ELECTROMAGNETIC INTERFERENCE SHIELD:

- REQUIREMENT IS TO REFLECT EM WAVES WITH SPECIFIED FREQUENCIES
- SHIELDING EFFECTIVENESS IS INVERSELY PROPORTIONAL TO SURFACE RESISTIVITY, i.e., LOW OHMS/SQUARE GIVES HIGH SHIELDING
- COMPROMISE IS FOR LOW RESISTIVITY WITH ACCEPTABLE TRANSMITTANCE

SPECIFYING AND SELECTING TRANSPARENT CONDUCTIVE COATINGS

FUNCTION

HEATER:

- REQUIREMENT IS FOR A RESISTANCE WHICH PERMITS ACHIEVING THE NEEDED POWER (DENSITY) FROM THE AVAILABLE VOLTAGE SOURCE
- TRANSMITTANCE CAN BE MAXIMIZED BY USE OF PART GEOMETRY AND CHOICE OF VOLTAGE SOURCE i.e. MORE THAN ONE OHMS/SQUARE CAN MEET RESISTANCE REQUIREMENT

ANTISTATIC:

- REQUIREMENT IS TO DISCHARGE STATIC CHARGE NON-DESTRUCTIVELY
- RESISTANCE CAN BE HIGH AND STILL ACHIEVE ADEQUATE DISCHARGE TIMES
- THUS, OHMS/SQUARE CAN BE HIGH, WITH ATTENDANT HIGH TRANSMITTANCE

SPECIFYING AND SELECTING TRANSPARENT CONDUCTIVE COATINGS

FUNCTION

HEAT MIRROR:

- REQUIREMENT IS FOR HIGH SOLAR REFLECTANCE, LOW INFRARED (IR) EMISSIVITY AND MEDIUM LUMINOUS TRANSMITTANCE
- HIGH FREE CARRIER DENSITY PRODUCES HIGH SOLAR AND INFRARED REFLECTANCE
- PLASMA FREQUENCY SHOULD IDEALLY BE AT EDGE OF VISIBLE/NEAR IR WAVEBANDS

CONDUCTIVE ANTIREFLECTION

- OPTICAL REQUIREMENT IS FOR LOW LUMINOUS REFLECTANCE AND LOW AVERAGE VISIBLE REFLECTANCE
- CONDUCTIVE REQUIREMENTS IS FOR ANTISTATIC AND/OR ELECTROMAGNETIC INTERFERENCE SHIELDING
- OPTICAL DESIGN DETERMINES TCC THICKNESS

TRANSPARENT CONDUCTIVE COATING DEPOSITION METHODS

EVAPORATION

THERMAL:

- NOBLE METALS (Ag, Au) AND TCO LIKE INDIUM OXIDE (IO), INDIUM TIN OXIDE (ITO) AND TIN OXIDE (TO) CAN BE DEPOSITED FROM REFRACTORY METAL BOATS, OR FILAMENTS AND FROM CERAMIC CRUCIBLES

- TYPICAL STARTING MATERIALS ARE METAL WIRES AND PIECES OR METAL OXIDE POWDERS (CHUNKS) AND PELLETS

- THE DIFFICULTY AND TEMPERATURE FOR EVAPORATION INCREASES WITH THE MATERIAL MELTING POINT

- OXYGEN BACKGROUND GAS USED FOR REACTIVE EVAPORATION OR TO MAKE UP FOR DISSOCIATION OF METAL OXIDES

TRANSPARENT CONDUCTIVE COATING DEPOSITION METHODS

EVAPORATION

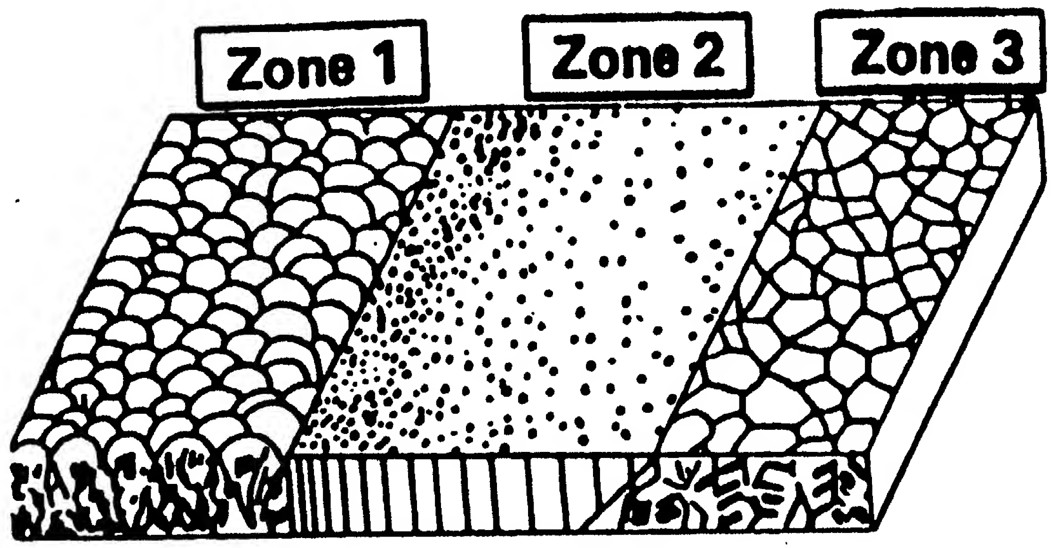
ELECTRON – BEAM:

- BOTH METALS AND METAL OXIDES CAN BE READILY EVAPORATED
- IO, ITO OR TO DEPOSITED WITH EQUAL EASY
- OXYGEN GAS USED FOR REACTIVE EVAPORATION OR TO MAKE UP FOR DISSOCIATION OF METAL OXIDES

PLASMA OR ION ASSISTED

- DEPOSITION RATES CAN BE INCREASED
- FILM DENSITY AND REFRACTIVE INDEX INCREASED

MICROSTRUCTURES OF EVAPORATED COATINGS



Zone 1: Porous, Low density, brittle coating.

Zone 2: Surface diffusion produces dense, columnar structure

Zone 3: Bulk diffusion produces recrystallized grains

B.A. Movchan and A.V. Demshishin, Fiz. Metal. Metalloved., 28, part 2:83 (1969)

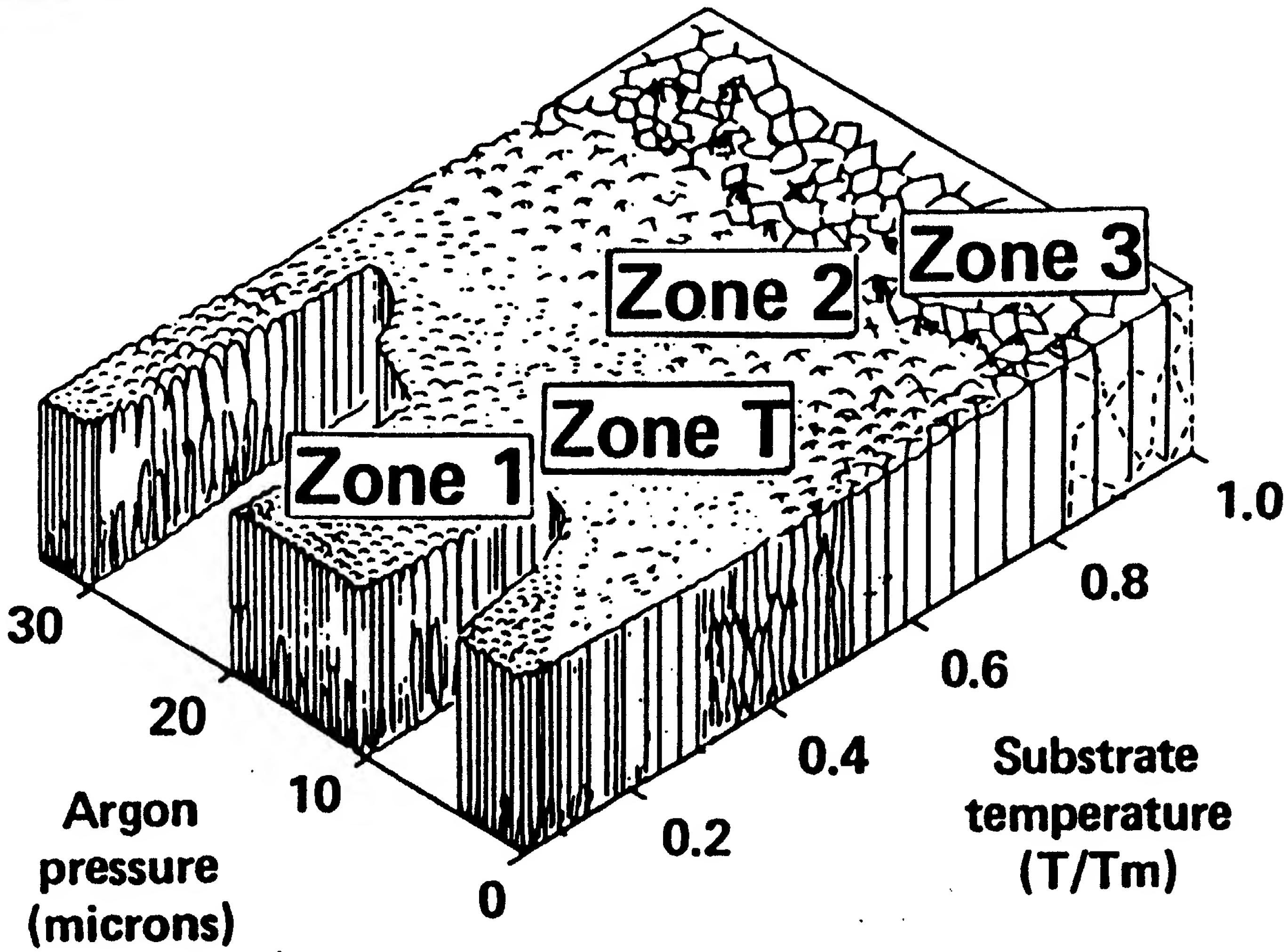
TRANSPARENT CONDUCTIVE COATING DEPOSITION METHODS

SPUTTERING

DC MAGNETRON – METALS

- HIGH DEPOSITION RATES
- DENSE FILMS
- BULK LIKE REFRACTIVE INDEX

THORNTON STRUCTURE ZONE MODEL FOR SPUTTERED COATINGS



from J.A. Thornton, J. Vac. Sci. Trchnol; 11:666 (1974)

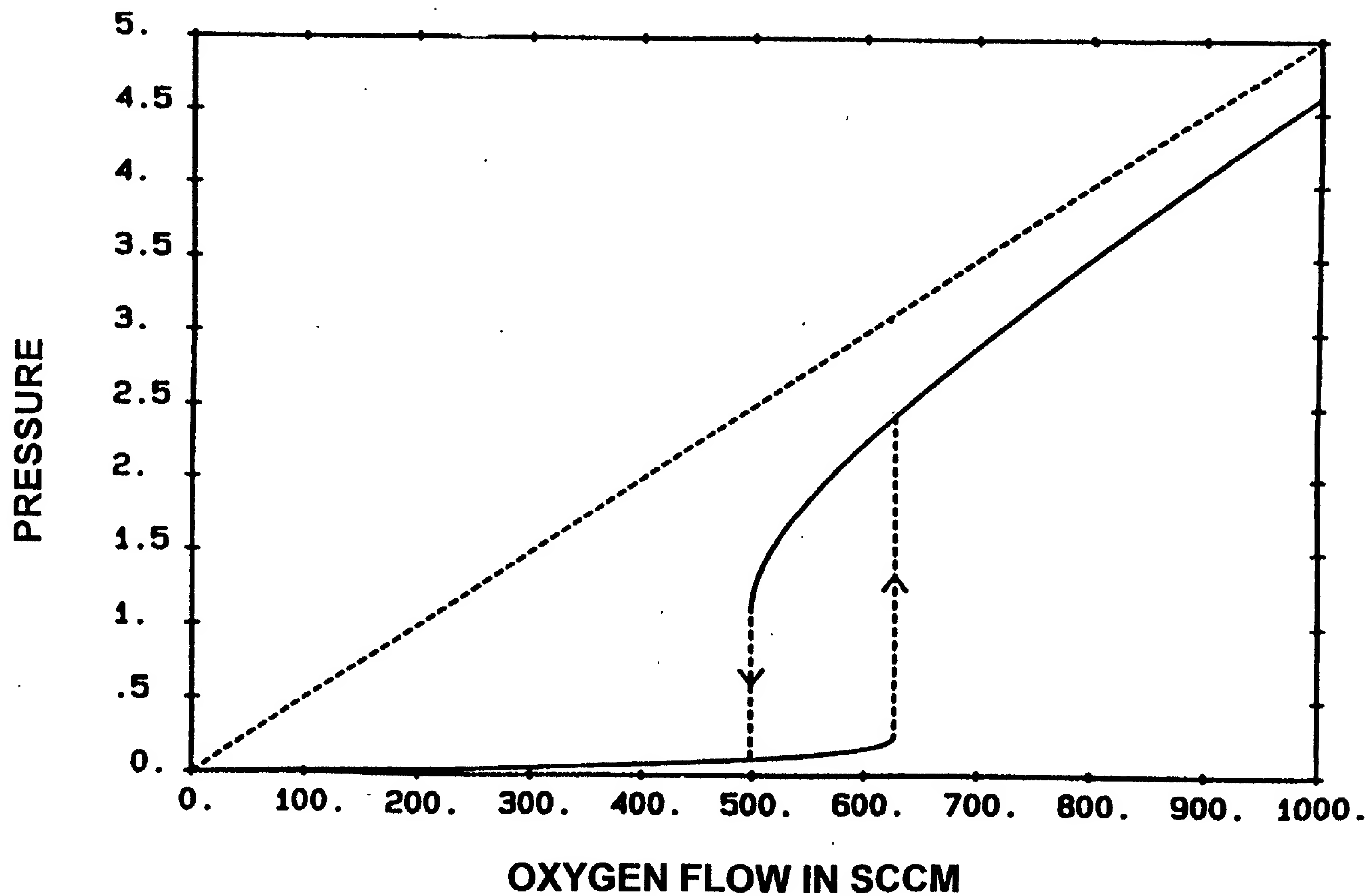
TRANSPARENT CONDUCTIVE COATING DEPOSITION METHODS

SPUTTERING

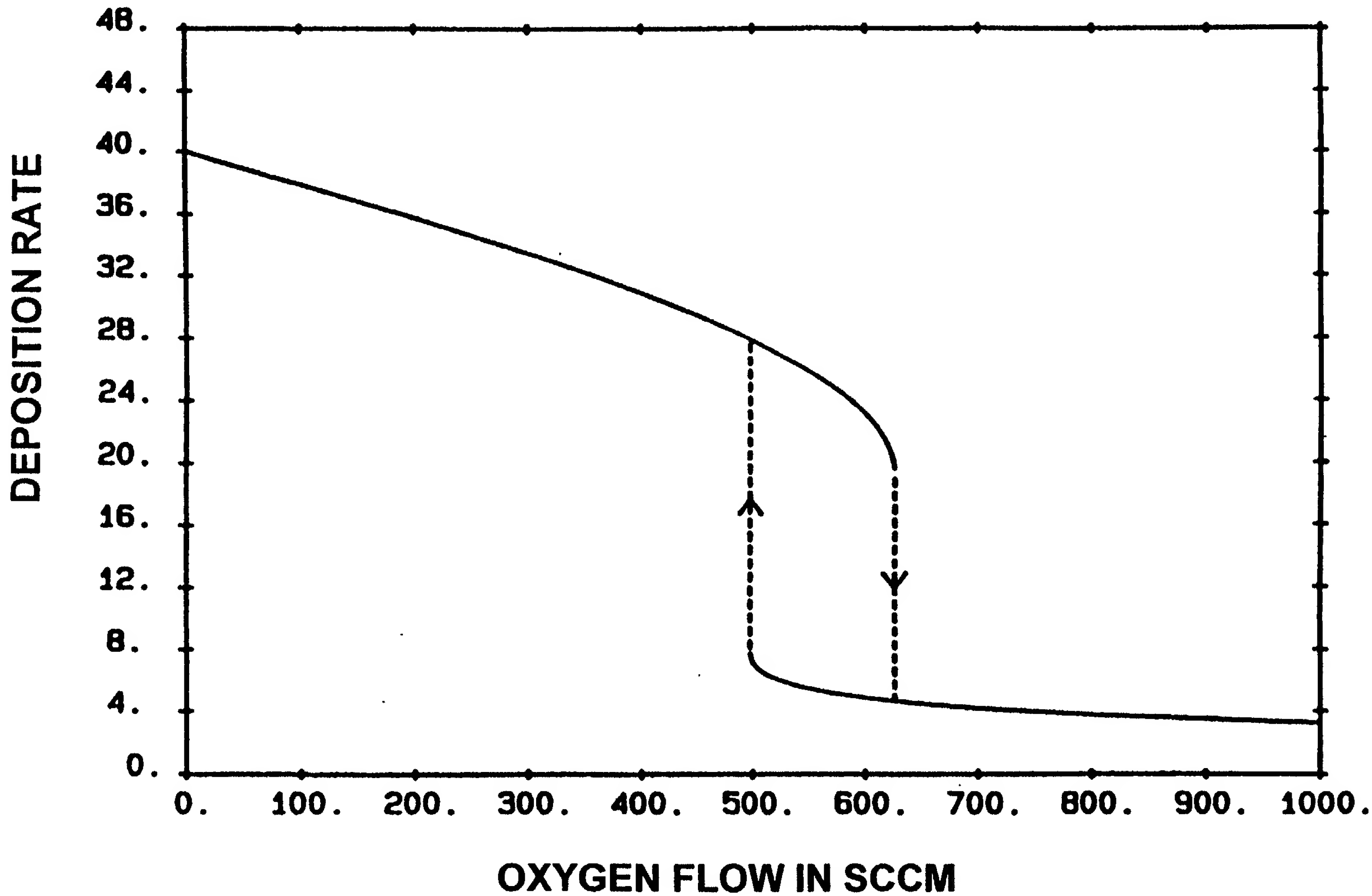
DC MAGNETRON - REACTIVE

- REACTIVE SPUTTERING FROM METALLIC TARGETS TO DEPOSIT IO, ITO, TO, ZINC OXIDE (ZO) ET AL
- HIGH DEPOSITION RATE IF TARGET IS KEPT FROM OXIDIZING
- ARCING AT OXIDIZED AREAS OF TARGET IS A PROBLEM

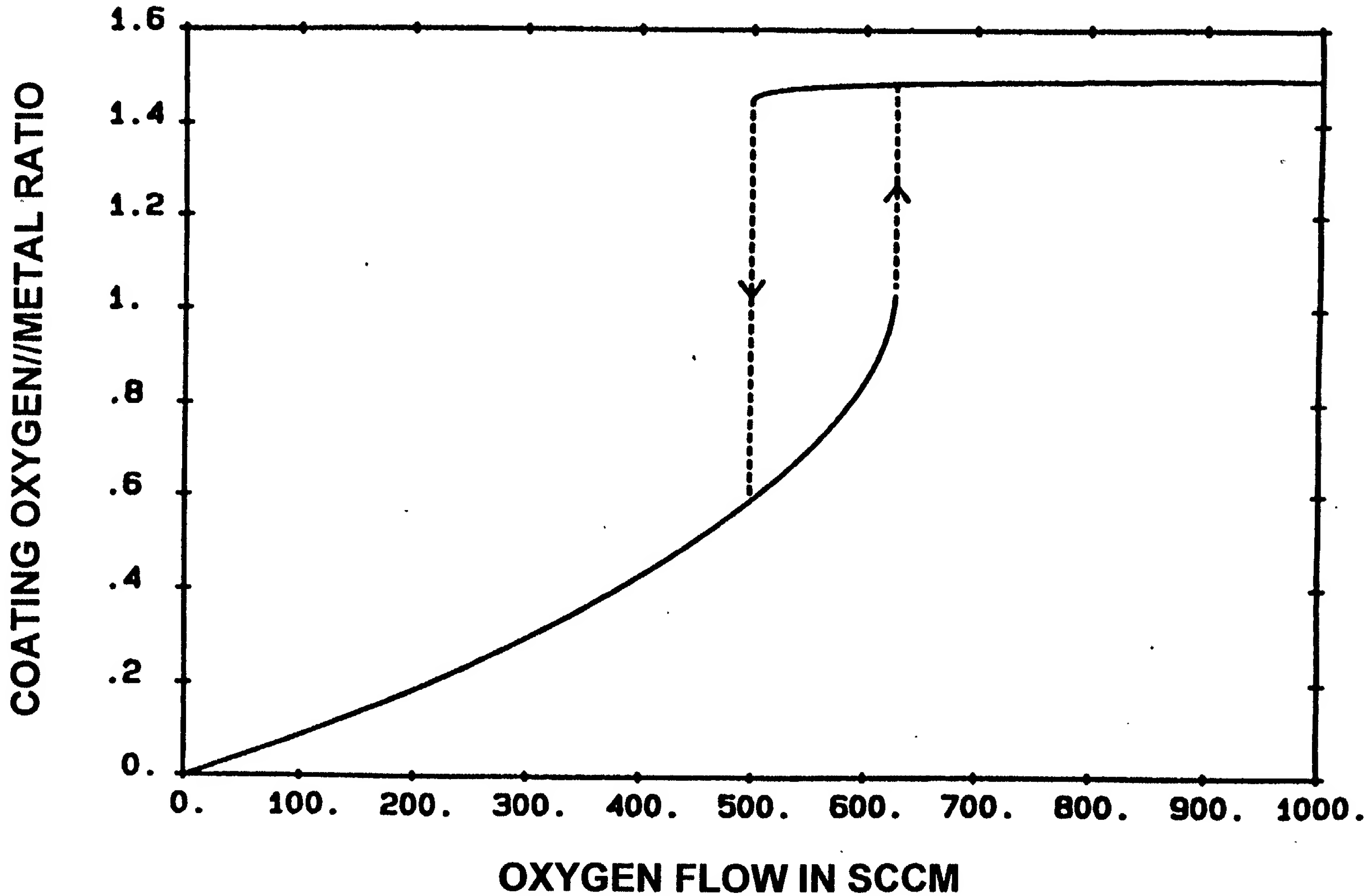
PRESSURE RESPONSE TO OXYGEN FLOW



DEPOSITION RATE RESPONSE TO OXYGEN FLOW



COATING OXYGEN/METAL RATIO RESPONSE TO OXYGEN FLOW



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TRANSPARENT CONDUCTIVE COATING DEPOSITION METHODS

SPUTTERING

DC MAGNETRON - SEMIREACTIVE

- SEMIREACTIVE SPUTTERING FROM CERAMIC TARGETS OF REDUCED IO, ITO, TO, ZO
- MUCH EASIER TO CONTROL THAN REACTIVE METAL PROCESS
- ARCING PROBLEM AND COATING DEFECTS REDUCED
- REQUIRES HIGHER POWER (DENSITY) THAN METAL TARGET FOR EQUIVALENT SPUTTERING RATES

TRANSPARENT CONDUCTIVE COATING DEPOSITION METHODS

SPUTTERING

RF SPUTTERING – DIODE OR MAGNETRON

- MAIN BENEFIT IS THAT TARGET MATERIALS NEED NOT HAVE DC CONDUCTIVITY
- MAIN DISADVANTAGE IS LOW DEPOSITION RATES
- EM SHIELDING OF EQUIPMENT REQUIRED
- SAFETY ISSUES

TRANSPARENT CONDUCTIVE COATING DEPOSITION METHODS

PYROLYSIS AND CHEMICAL VAPOR DEPOSITION (CVD)

PYROLYSIS - LIQUID

- CAN USE LOW COST MATERIALS
- MATERIALS AND REACTION PRODUCTS CAN BE HAZARDOUS
- DEPOSITION POSSIBLE AT ATMOSPHERIC PRESSURE
- TYPICALLY SPRAY PROCESS
- HIGH TEMPERATURE PROCESS

TRANSPARENT CONDUCTIVE COATING DEPOSITION METHODS

POST DEPOSITION PROCESSES

TCO POST PROCESSING

- BAKING IN VACUUM CAN REDUCE RESISTIVITY, IMPROVE CRYSTALLINITY, REDUCE INTRINSIC COATING STRESS
- BAKING IN OXIDIZING GAS CAN REDUCE ABSORPTION, INCREASE TRANSMITTANCE, IMPROVE DURABILITY, INCREASE RESISTIVITY, INCREASE REFRACTIVE INDEX
- BAKING IN AN INERT GAS CAN INCREASE REACTIVE INDEX, REDUCE COATING STRESS AND IMPROVE CRYSTALLINITY
- BAKING IN A REDUCING GAS CAN LOWER RESISTIVITY IMPROVE CRYSTALLINITY, REDUCE COATING STRESS, LOWER REFRACTIVE INDEX AND INCREASE ABSORPTION

TRANSPARENT CONDUCTIVE COATING DEPOSITION METHODS

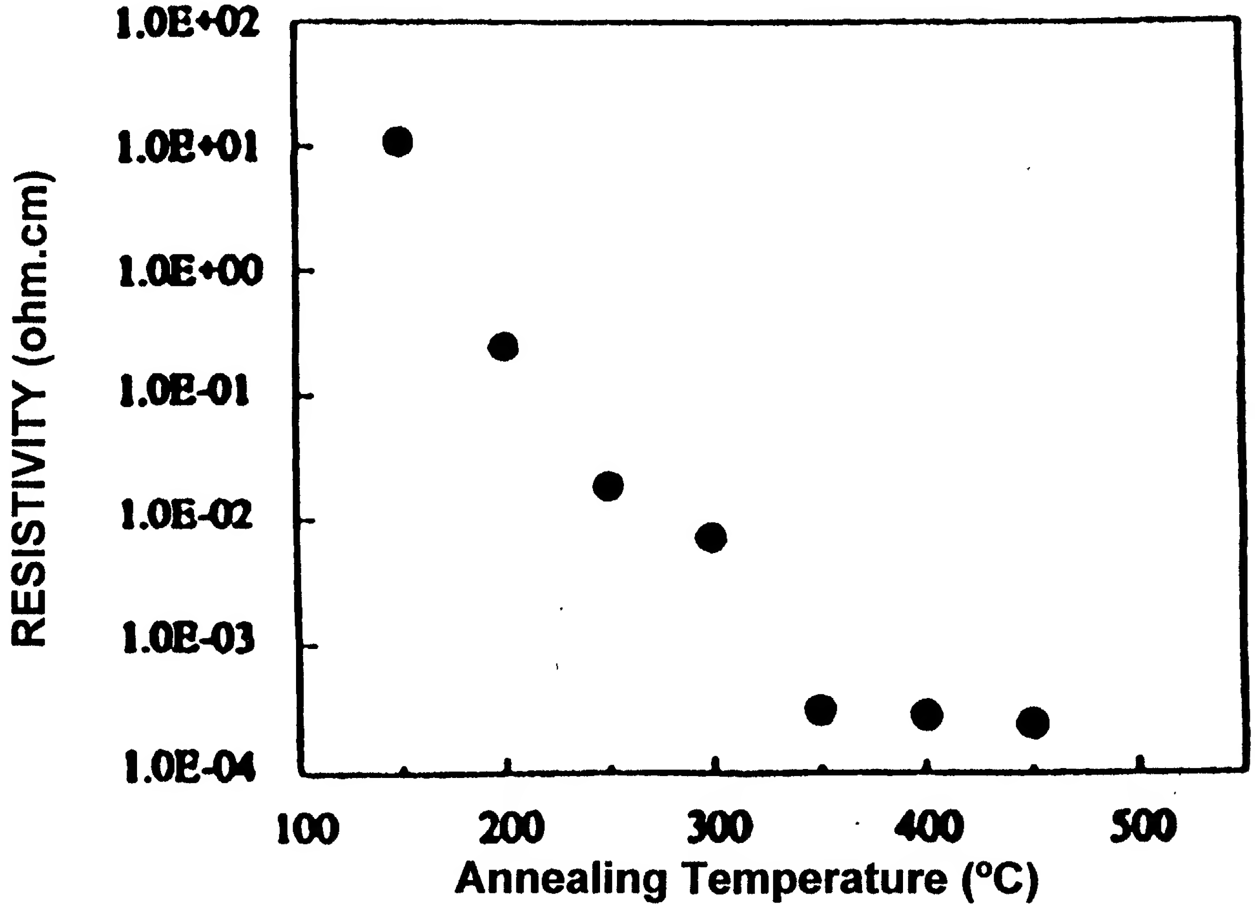
PYROLYSIS AND CHEMICAL VAPOR DEPOSITION (CVD)

LOW PRESSURE CVD - VAPOR

- COATS ALL EXPOSED SURFACES
- COATINGS ARE VERY DURABLE
- DEPOSITION RATES CAN BE VERY HIGH
- MATERIALS AND REACTION PRODUCTS CAN BE HAZARDOUS
- HIGH TEMPERATURE PROCESS
- PLASMA ENHANCEMENT CAN REDUCE PROCESS TEMPERATURE

TRANSPARENT CONDUCTIVE COATING DEPOSTION METHODS

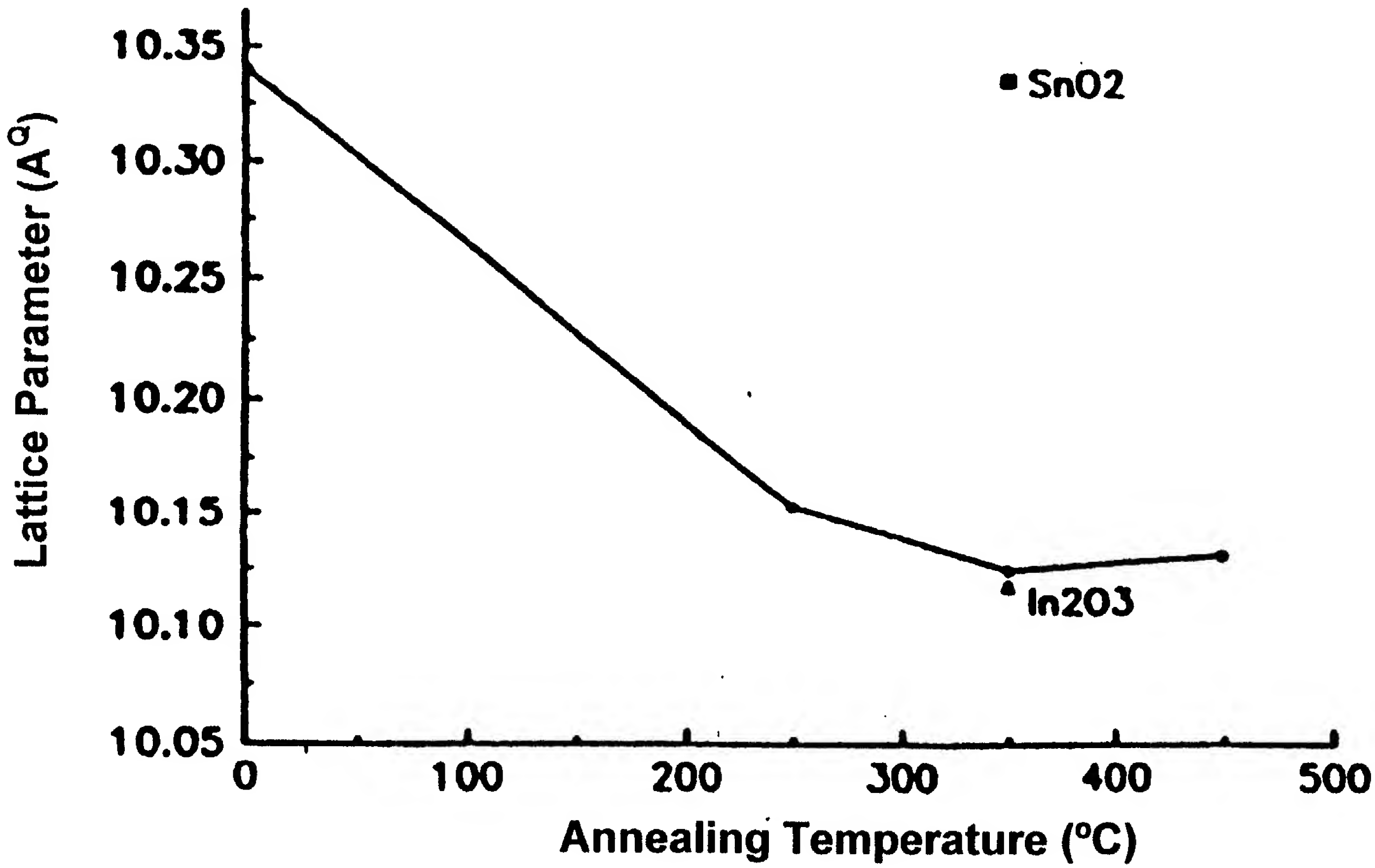
POST DEPOSTION PROCESSES



Surface Resistivity Versus Vacuum Annealing Temperature (25 min.) for Sputtered ITO
(From M. A. Martines, et al, Thin Solid Films, 269, (1995) 80-84)

TRANSPARENT CONDUCTIVE COATING DEPOSITION METHODS

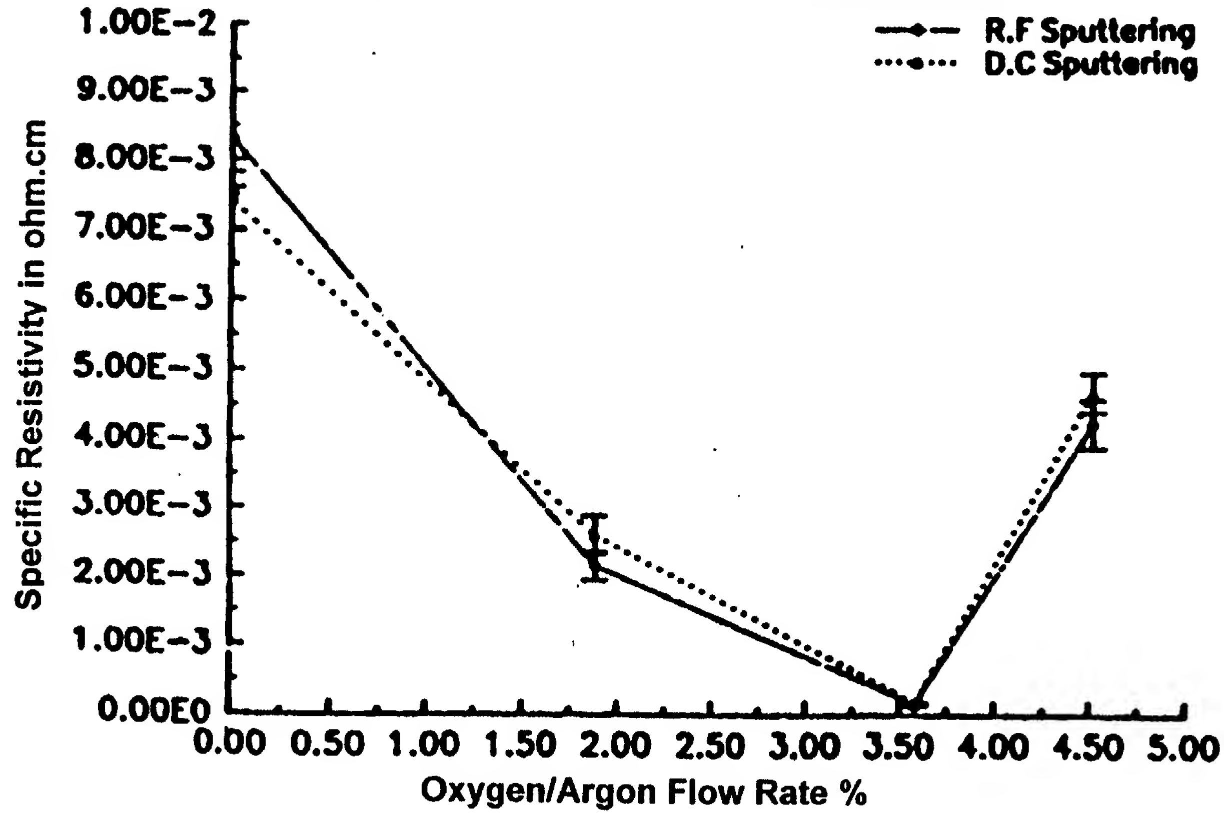
POST DEPOSTION PROCESSES



Surface Resistivity Versus Annealing Temperature (24 min.) for Sputtered ITO
(From M. A. Martines, et al, Thin Solid Films, 269, (1995) 80-84)

TRANSPARENT CONDUCTIVE COATING DEPOSITION METHODS

POST DEPOSITION PROCESSES



Surface Resistivity for Sputtered ITO Films Annealed (2 hours in air) at 350°C as a Function of Oxygen/Argon Flow Rate during Sputtering

(From R. N. Joshi, et al, Thin Solid Films, 257, (1995) 32-35)

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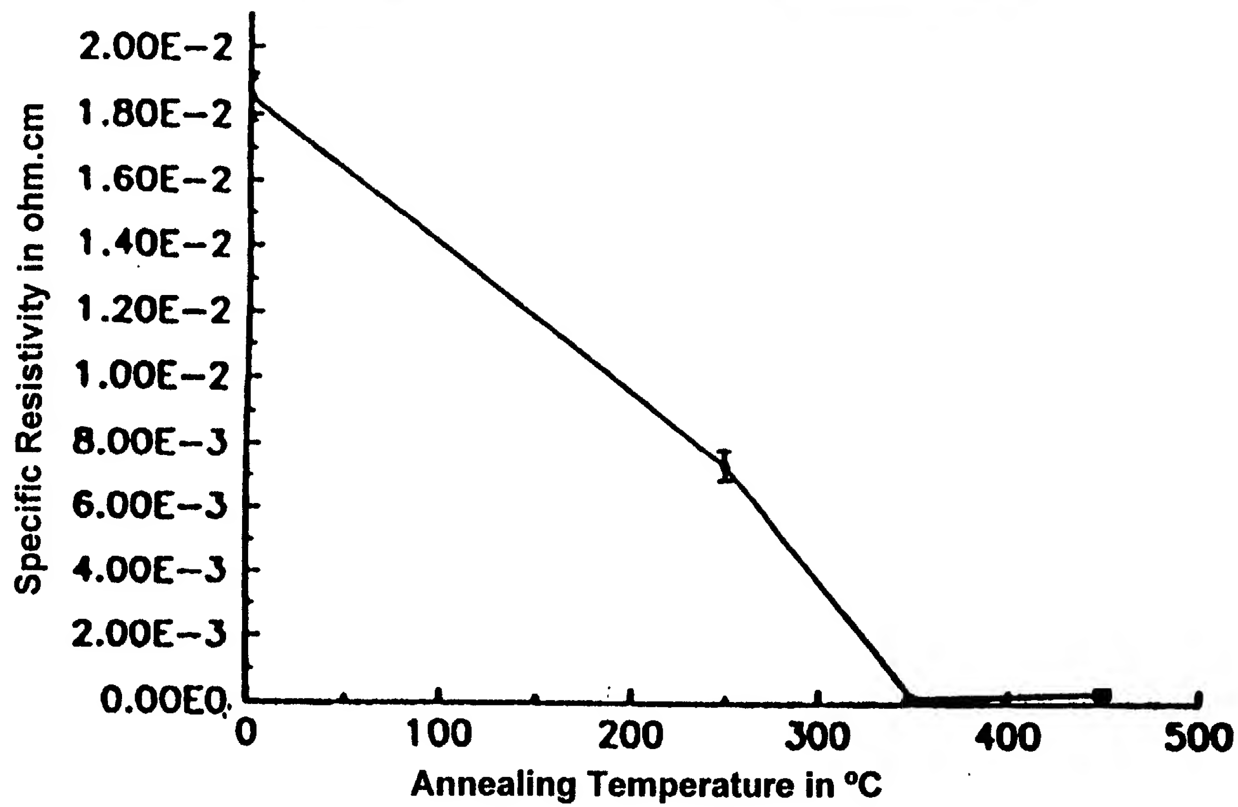
TRANSPARENT CONDUCTIVE COATING DEPOSITION METHODS

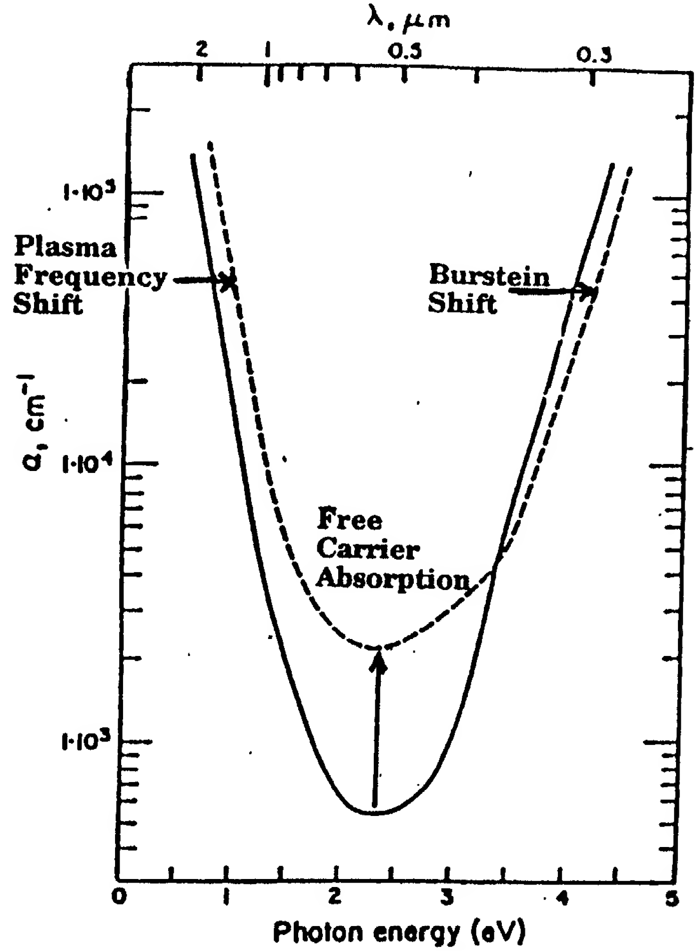
POST DEPOSITION PROCESSES



Surface Resistivity Versus Annealing Temperature (2 hours in air) for r.f. Sputtered ITO
(From R. N. Joshi, et al, <u>Thin Solid Films</u>, 257, (1995) 32-35)

T04280" 8006E660

Absorption as a Function of Photon Energy



Solid line: As deposited ITO film. (N = 5.8 x 10^{20} / cm^3)
Broken line: After 30 min. at 400 C in N_2 + 10% H_2.
(N = 11.2 x 10^{20} / cm^3)

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IMPORTANT TCO VACUUM PROCESS PARAMETERS

<u>SUBSTRATE TEMPERATURE</u>

- MAXIMIZING SUBSTRATE TEMPERATURE WILL IMPROVE CRYSTALLINITY WHICH INCREASE ELECTRON MOBILITY AND SCATTERING TIME

- A THRESHOLD TEMPERATURE IS REQUIRED TO ACTIVATE METAL, e.g. Sn, DOPANTS

<u>DEPOSITION RATE</u>

- LOW PRODUCT COST DICTATES HIGH DEPOSITION RATES

- FOR SPUTTERING, HIGH RATES REQUIRES OPERATING IN THE METAL MODE

- HIGH DEPOSITION RATES MUST BE SUPPORTED BY HIGH REACTION RATES BETWEEN METAL ATOMS OR IONS AND OXYGEN ATOMS OR IONS

IMPORTANT TCO VACUUM PROCESS PARAMETERS

OXYGEN PARTIAL PRESSURE

- BECAUSE OXYGEN DEFICIENCY IS THE MAJOR CONTROL OF CONDUCTIVITY AND ABSORPTION, CONTROL IS CRITICAL

CHAMBER PRESSURE

- LOWER CHAMBER PRESSURE MEANS ATOMS ARRIVE AT SUBSTRATE WITH MORE KINETIC ENERGY WHICH IMPROVES CRYSTALLINIETY AND REDUCES DEFECTS

- IF PRESSURE IS TOO LOW, DEPOSITED FILM WILL BE REDUCED (METALLIC)

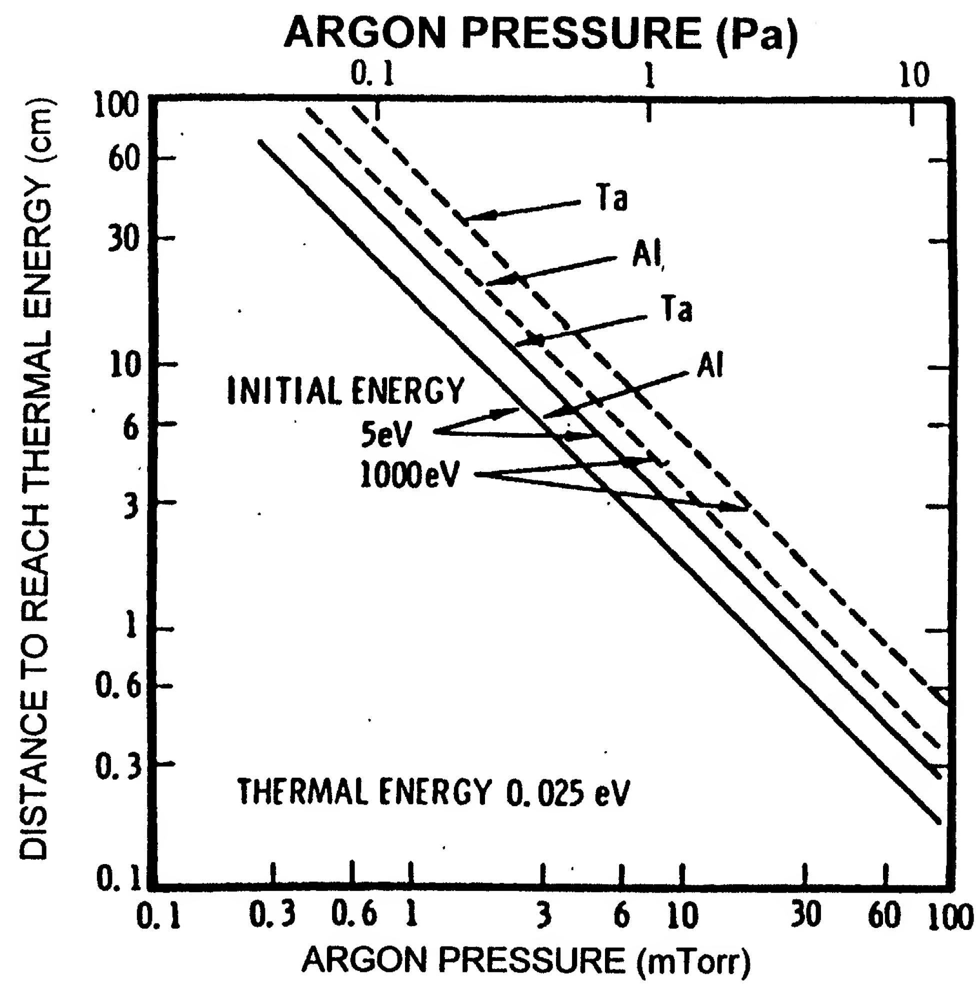
- IF PRESSURE IS TOO LOW, A SPUTTERING PROCESS CAN NOT BE MAINTAINED

- LOW CHAMBER PRESSURE PRODUCES MORE LINE-OF-SIGHT DEPOSITION

IMPORTANT TCO VACUUM PROCESS PARAMETERS

<u>SOURCE TO SUBSTRATE DISTANCE</u>

- SMALL SEPARATION PRODUCES MORE SUBSTRATE HEATING
- SMALL SEPARATION MEANS ATOMS AND IONS ARRIVE WITH MORE KINETIC ENERGY
- LARGE SEPARATION PRODUCES MORE LINE-OF-SIGHT DEPOSITION
- LARGE SEPARATION ALLOWS MORE TIME FOR REACTION WITH OXYGEN IN CHAMBER



Maximum distance from the target at which sputtered Al and Ta atoms of different initial energies are thermalized in Ar at various pressures. Thermalized energy assumed to be 0.025 eV.

W.D. Westwood, J. Vac. Sci. Technol. 15, 188 (1978).

DEVELOPING AN ITO PROCESS

SELECTING THE DEPOSITION PROCESS

- DEPOSITION PROCESS MAY BE DICTATED BY AVAILABLE EQUIPMENT
- COATING APPLICATION MAY FAVOR A PARTICULAR DEPOSITION TECHNOLOGY
- TYPE OF SUBSTRATE CAN INFLUENCE DEPOSITION PROCESS CHOICE
- COATING DENSITY AND DURABILITY MAY INFLUENCE PROCESS CHOICE

DEVELOPING AN ITO PROCESS

<u>STARTING MATERIAL CHOICE</u>

- AFTER DEPOSITION PROCESS IS CHOSEN, STARTING MATERIAL CHOICES ARE REDUCED
- COST/PERFORMANCE CONSIDERATION
- CONVENIENCE AND AVAILABILITY ISSUES
- APPLICATION REQUIREMENTS USUALLY MAJOR FACTOR IN SELECTING TYPE AND FORM OF STARTING MATERIAL

DEVELOPING AN ITO PROCESS

<u>CHOOSING SUBSTRATE TEMPERATURE</u>

- FROM COATING PERFORMANCE CONSIDERATIONS ALONE - "HOTTER IS BETTER"
- EQUIPMENT LIMITATIONS MAY DICTATE MAXIMUM TEMPERATURE
- THERMAL LIMITATIONS OF SUBSTRATE MAY DETERMINE PROCESS TEMPERATURE
- COST/PERFORMANCE TRADE-OFFS CAN INFLUENCE TEMPERATURE SELECTION

DEVELOPING AN ITO PROCESS

<u>SELECTING ITO THICKNESS</u>

- ITO THICKNESS RANGE USUALLY DETERMINED BY COATING FUNCTION
- OPTICAL REQUIREMENTS CAN DETERMINE ALLOWED THICKNESS(ES)
- OPTICAL VERSUS ELECTRICAL PERFORMANCE TRADE OFF
- COST, POST PROCESSING SPEED, COATING STRESS AND DURABILITY ARE FACTORS
- COATING ENVIRONMENTAL REQUIREMENTS, e.g. TEMPERATURE CYCLING, CAN INFLUENCE CHOICE

DEVELOPING AN ITO PROCESS

DETERMINING THE RESISTIVITY "WELL"

- NOW THAT THE TYPE OF DEPOSITION PROCESS, STARTING MATERIAL, SUBSTRATE TEMPERATURE AND ITO THICKNESS HAVE BEEN SELECTED, DETERMINE THE INFLUENCE OF OXYGEN FLOW RATE/PARTIAL PRESSURE ON (SURFACE) RESISTIVITY

- AT LOW CHAMBER PRESSURE, WITH A CONSTANT DEPOSITION RATE (POWER SETTING) ADD OXYGEN UNTIL CHAMBER PRESSURE JUST BEGINS TO RISE, (OPEN SHUTTER, CHANGE MONITOR CHIP), DEPOSIT A SAMPLE UNTIL DESIRED THICKNESS IS ACHIEVED

- IF POSSIBLE, CLOSE SHUTTER, CHANGE CHIP, INCREMENT OXYGEN FLOW RATE AND REPEAT DEPOSITION STEP

- OTHERWISE, BREAK VACUUM REMOVE PART, RELOAD CHAMBER AND REPEAT DEPOSITION STEP AT NEW OXYGEN FLOW RATE

- AFTER SEVERAL DEPOSITIONS AT HIGHER AND LOWER OXYGEN FLOW RATES, PLOT MEASURED RESISTIVITY VERSUS OXYGEN FLOW RATE TO DETERMINE "WELL"

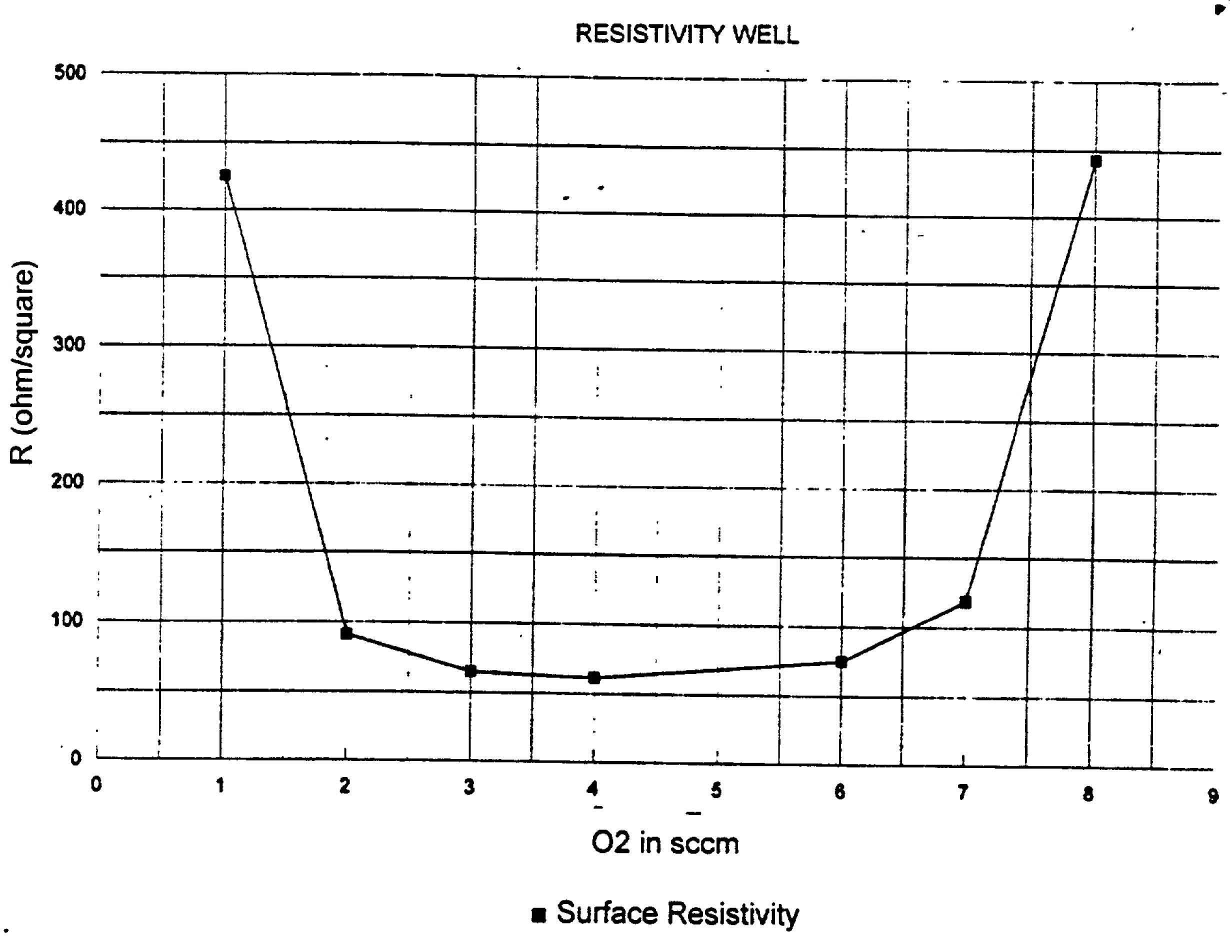
INDIUM TIN OXIDE CERAMIC TARGET

TARGET: 90 wt. % In203 / 10 wt. % SnO2 — Date: 04-09-96

SUBSTRATE: Glass Slide

CONDITIONS:
no heat
power .50 KW
speed 5.75 inch/min.
total flow 50 sccm
pressure 1.8 – 1.9 microns

O2 (sccm)	1	2	3	4	6	7	8
R (ohms/square)	425	91.3	64.9	61.05	75	119	443
%T vis (Luminous)	66.8	80.6	84.9	87.1	87.8	86.3	83.3
thickness (nm, slide)	102.6	96.3	107.5	94.3	93.3	99.9	100.5
rho (x1.0E-4 ohm-cm)	43.6	8.8	7.0	5.8	7.0	11.9	44.5



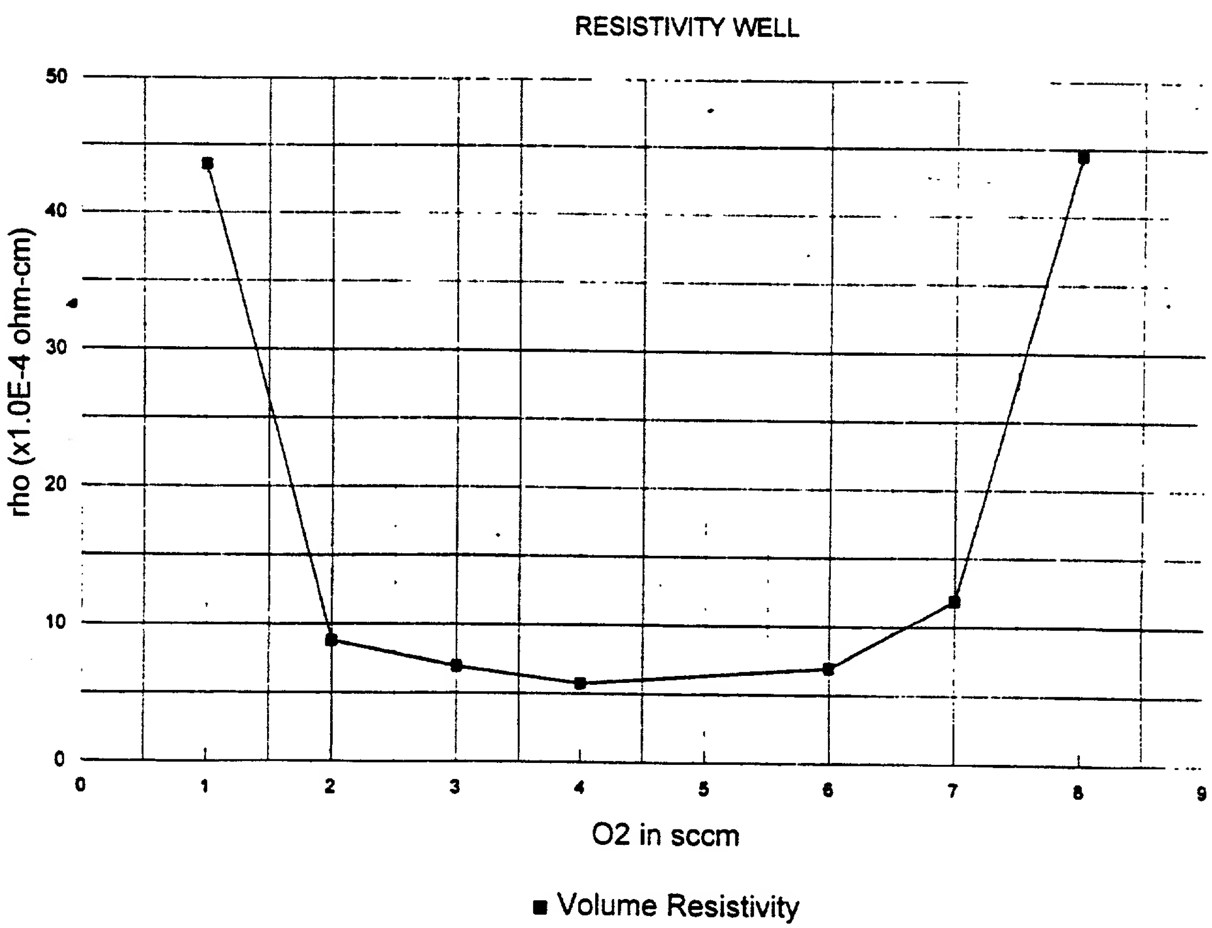
INDIUM TIN OXIDE CERAMIC TARGET

TARGET: 90 wt. % In203 / 10 wt. % SnO2 — Date: 04-09-96

SUBSTRATE: Glass Slide

CONDITIONS:
no heat
power .50 KW
speed 5.75 inch/min.
total flow 50 sccm
pressure 1.8 – 1.9 microns

O2 (sccm)	1	2	3	4	6	7	8
R (ohms/square)	425	91.3	64.9	61.1	75	119	443
%T vis (Luminous)	66.8	80.6	84.9	87.1	87.8	86.3	83.3
thickness (nm, slide)	102.6	96.3	107.5	94.3	93.3	99.9	100.5
rho (x1.0E-4 ohm-cm)	43.6	8.8	7.0	5.8	7.0	11.9	44.5



DEVELOPING AN ITO PROCESS

SELECTING OPTICAL VERSUS ELECTRICAL PERFORMANCE

- DETERMINE SPECTRAL TRANSMITTANCE, REFLECTANCE AND ABSORPTANCE OF COATINGS DEPOSITED TO DETERMINE RESISTIVITY "WELL"

- CALCULATE INTEGRATED OPTICAL VALUES OF INTEREST TO APPLICATION, e.g., LUMINOUS TRANSMITTANCE, FOR EACH SAMPLE AND PLOT VERSUS OXYGEN FLOW RATES

- FROM PLOTS OF SPECTRAL AND INTEGRATED OPTICAL VALUES, AND RESISTIVITY, SELECT FLOW RATE (PRESSURE) FOR PROCESS WHICH OPTIMIZES COMPROMISE AMONG REQUIREMENTS

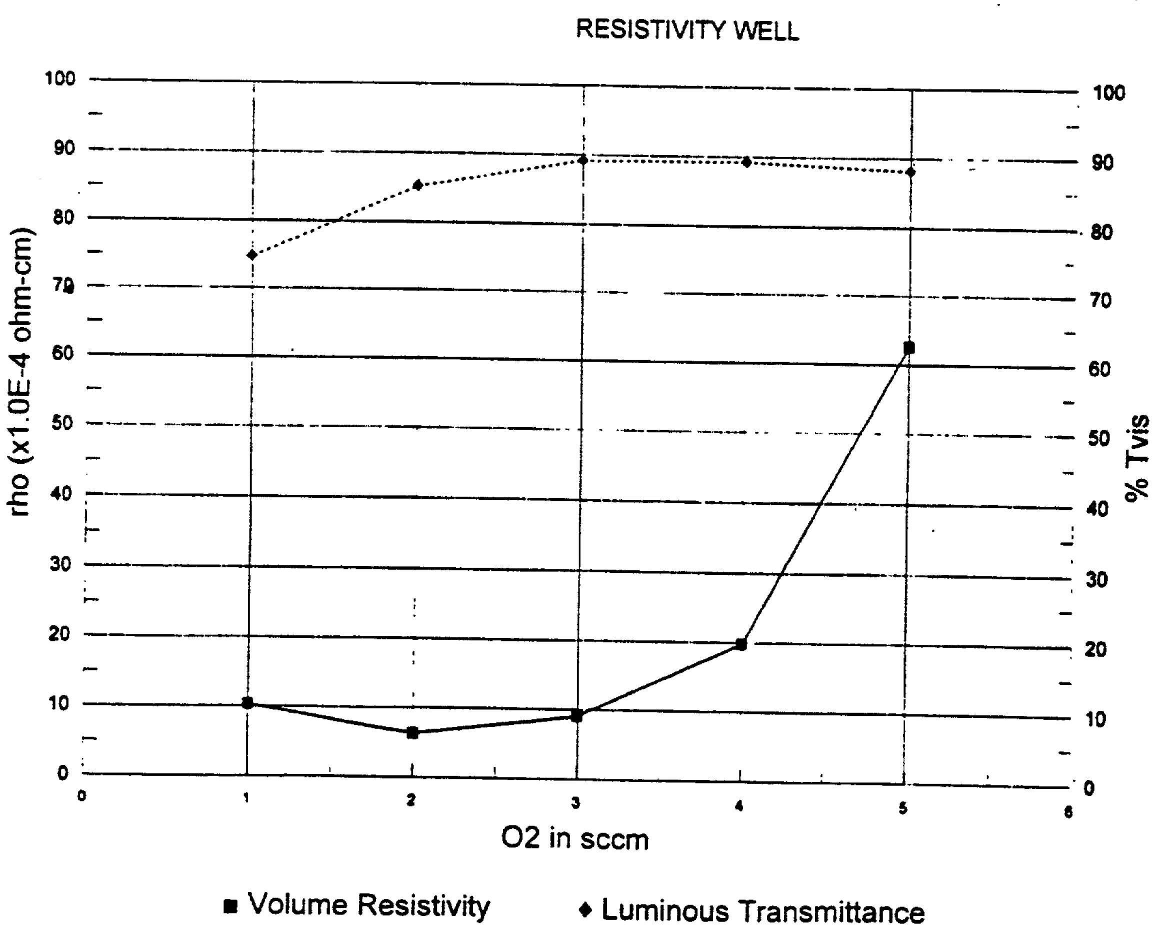
INDIUM TIN OXIDE CERAMIC TARGET

TARGET: 90 wt. % In203 / 10 wt. % SnO2 Date: 04-03-96

SUBSTRATE: Glass Slide

CONDITIONS:
no heat
power .50 KW
speed 5.75 inch/min.
total flow 50 sccm
pressure 2.0 microns

O2 (sccm)	1	2	3	4	5
R (ohms/square)	102	56.1	67	147.5	492
%T vis (Luminous)	74.7	85.3	89.2	89.3	88.2
thickness (nm, slide)	100.9	113.1	135.7	133.9	127.3
rho (x1.0E-4 ohm-cm)	10.3	6.3	9.1	19.8	62.6



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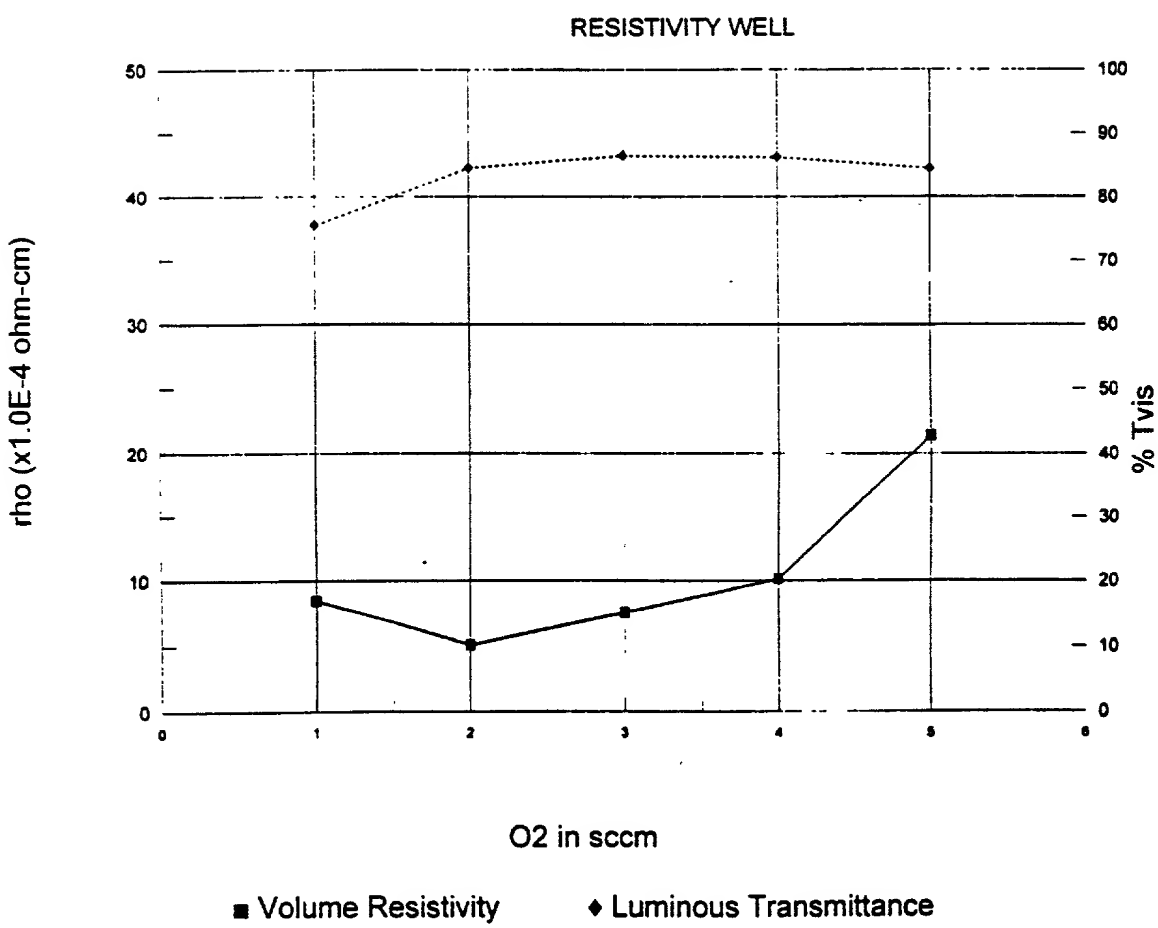
INDIUM TIN OXIDE CERAMIC TARGET

TARGET: 90 wt. % In203 / 10 wt. % SnO2 Date: 04-03-96

SUBSTRATE: ICI 725 PET

CONDITIONS:
no heat
power .50 KW
speed 5.75 inch/min.
total flow 50 sccm
pressure 2.0 microns

O2 (sccm)	1	2	3	4	5
R (ohms/square)	83.9	45.2	55.6	75.7	168.3
%T vis (Luminous)	75.5	84.6	86.5	86.3	84.5
thickness (nm, slide)	100.9	113.1	135.8	133.9	127.3
rho (x1.0E-4 ohm-cm)	8.5	5.1	7.6	10.1	21.4



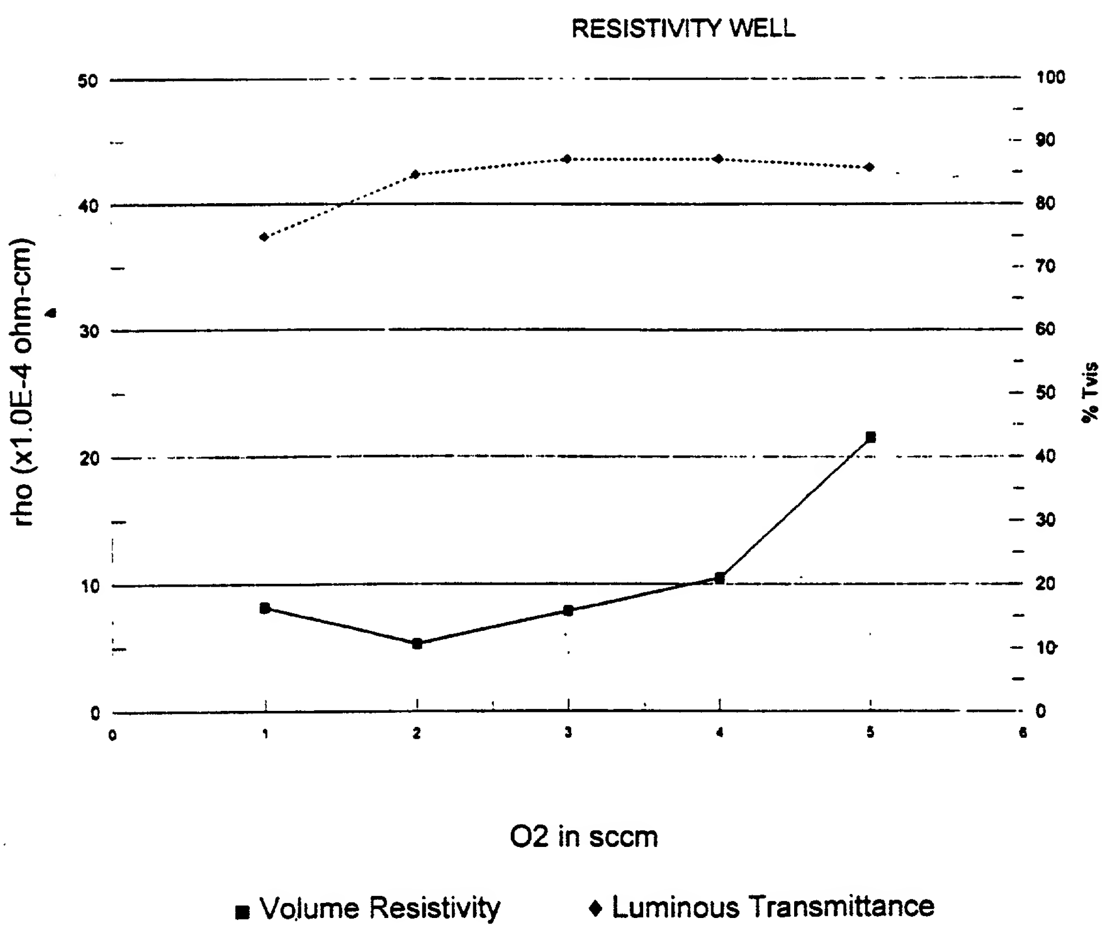
INDIUM TIN OXIDE CERAMIC TARGET

TARGET: 90 wt. % In203 / 10 wt. % SnO2 — Date: 04-03-96

SUBSTRATE: Hardcoat PET

CONDITIONS:
no heat
power .50 KW
speed 5.75 inch/min.
total flow 50 sccm
pressure 2.0 microns

O2 (sccm)	1	2	3	4	5
R (ohms/square)	81.5	46.9	58.2	78.4	168.9
%T vis (Luminous)	74.9	84.7	87.2	87.2	85.8
thickness (nm, slide)	100.9	113.1	135.7	133.9	127.3
rho (x1.0E-4 ohm-cm)	8.2	5.3	7.9	10.5	21.5



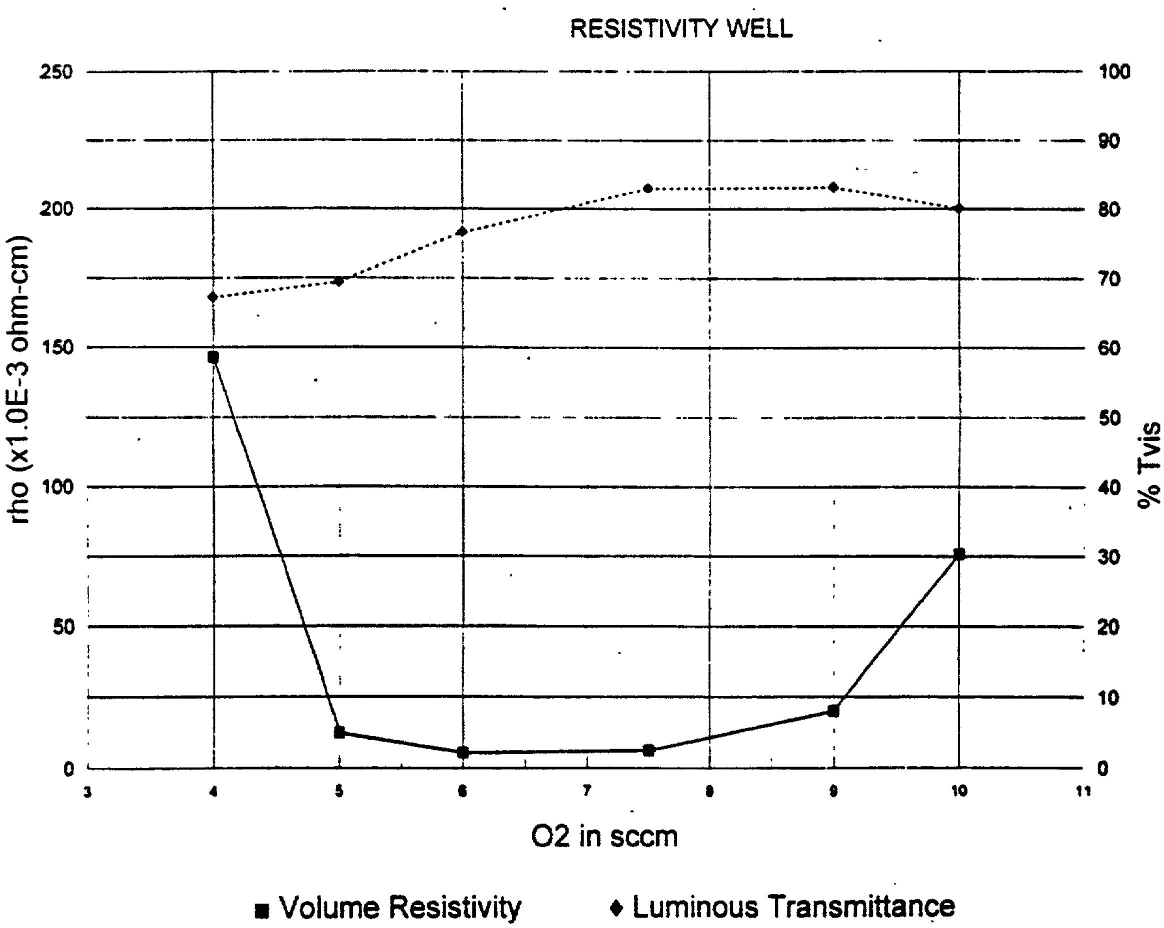
TIN OXIDE CERAMIC TARGET

TARGET: 98 wt. % SnO_2 / 2 wt.% Sb_2O_3 Date: 04-09-96

SUBSTRATE: ICI 725 PET

CONDITIONS:
no heat
power .50 KW
speed 5.75 inch/min.
total flow 50 sccm
pressure 1.8 – 1.9 microns

O2 (sccm)	4	5	6	7.5	9	10
R (ohms/square)	4710	420	183	214	714	3000
%T vis (Luminous)	67.2	69.4	76.6	83	83.2	80.1
thickness (nm, slide)	311	298.0	298.7	294.3	283.1	252.6
rho (x1.0E-3 ohm-cm)	146.5	12.5	5.5	6.3	20.2	75.8



Zinc TIN OXIDE CERAMIC TARGET

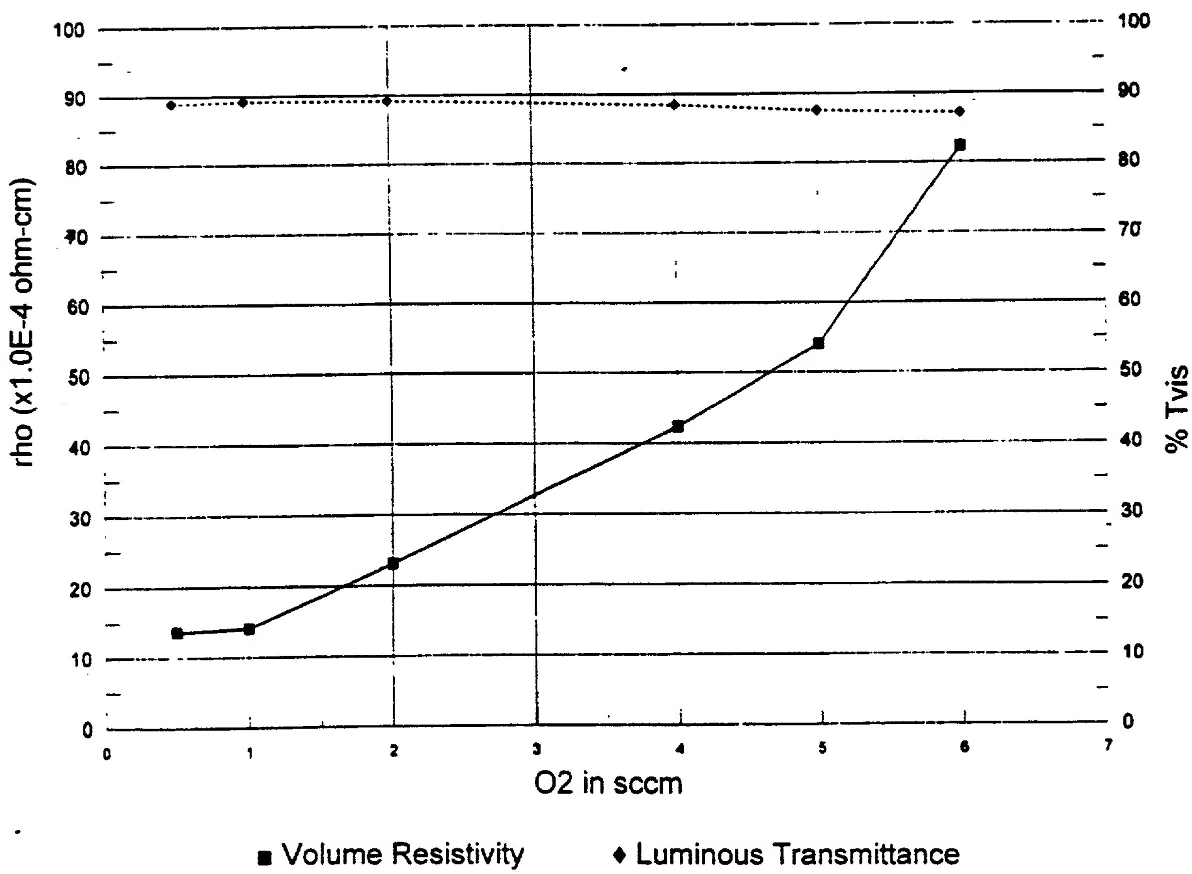
TARGET: 98 wt. % ZnO / 2 wt.% Al203 Date: 04-09-96

SUBSTRATE: ICI 725 PET

CONDITIONS:
no heat
power .50 KW
speed 5.75 inch/min.
total flow 50 sccm
pressure 1.8 – 1.9 microns

O2 (sccm)	0.5	1	2	4	5	6
R (ohms/square)	124.4	120.9	126.3	211	295	415
%T vis (Luminous)	88.9	89.2	89.2	88.4	87.5	87.1
thickness (nm, slide)	109.9	116.8	183.0	200.9	183.5	198.4
rho (x1.0E-4 ohm-cm)	13.7	14.1	23.1	42.4	54.1	82.3

RESISTIVITY WELL



DEVELOPING AN ITO PROCESS

MINIMIZING ABSORPTION

- CALCULATE SPECTRAL ABSORPTION COEFFICIENTS FROM MEASURED DATA ON RESISTIVITY "WELL" SAMPLES
- PLOT SPECTRAL ABSORPTION COEFFICIENTS VERSUS WAVELENGTH WITH OXYGEN FLOW RATE AS A PARAMETER
- FOR APPLICATIONS WHERE A SINGLE WAVELENGTH IS DOMINATE PLOT THAT ABSORPTION COEFFICIENT VERSUS FLOW RATE
- SELECT FLOW RATE FOR PROCESS WHICH MINIMIZES ABSORPTION COEFFICIENT NEAR RESISTIVITY MINIMUM

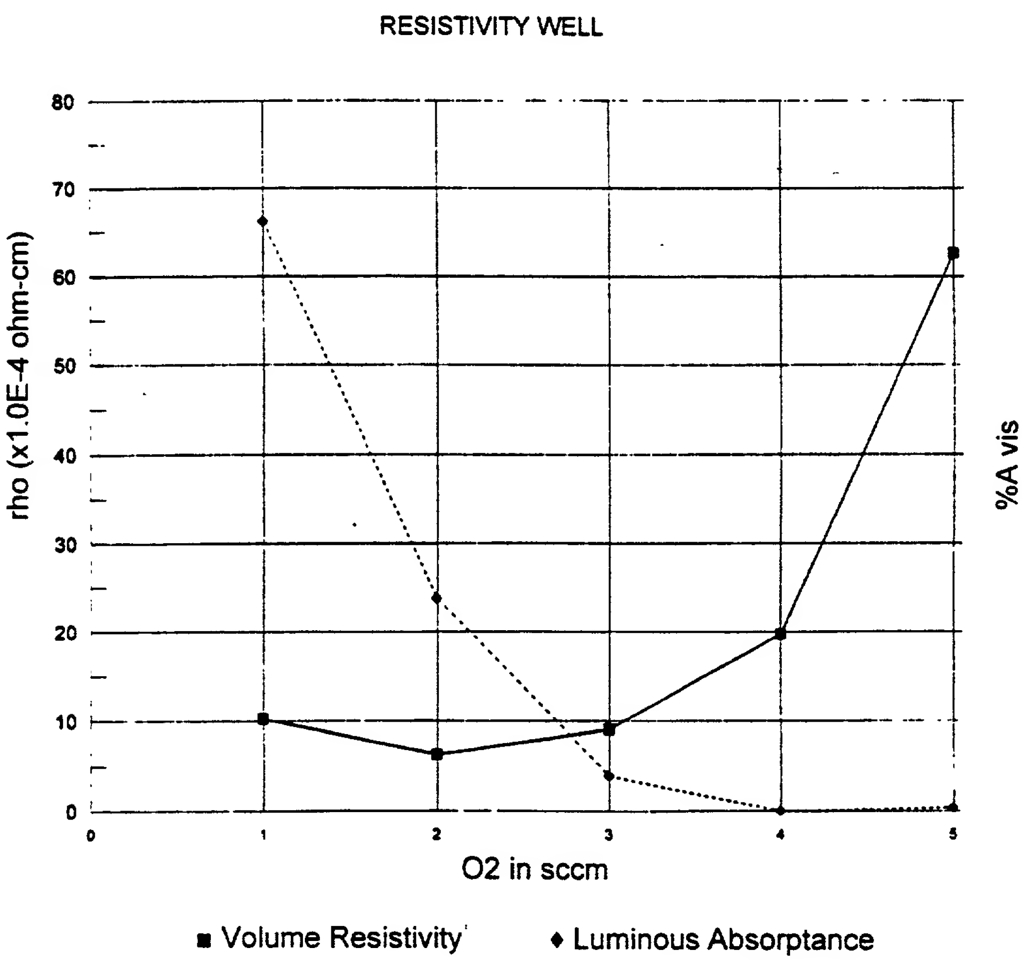
INDIUM TIN OXIDE CERAMIC TARGET

TARGET: 90 wt. % In203 / 10 wt.% SnO2 Date: 04-09-96

SUBSTRATE: Glass Slide

CONDITIONS: no heat
power .50 KW
speed 5.75 inch/min.
total flow 50 sccm
pressure 1.8 – 1.9 microns

O2 (sccm	1	2	3	4	5
R (ohms/square)	102	56.1	67	147.5	492
%T vis (Luminous)	74.7	85.3	89.2	89.3	88.2
thickness (nm, slide)	100.9	113.1	135.7	133.9	127.3
rho (x1.0E-4 ohm-cm)	10.3	6.3	9.1	19.8	62.6
%A vis (Luminous)	13.24	4.75	0.78	0	0.08



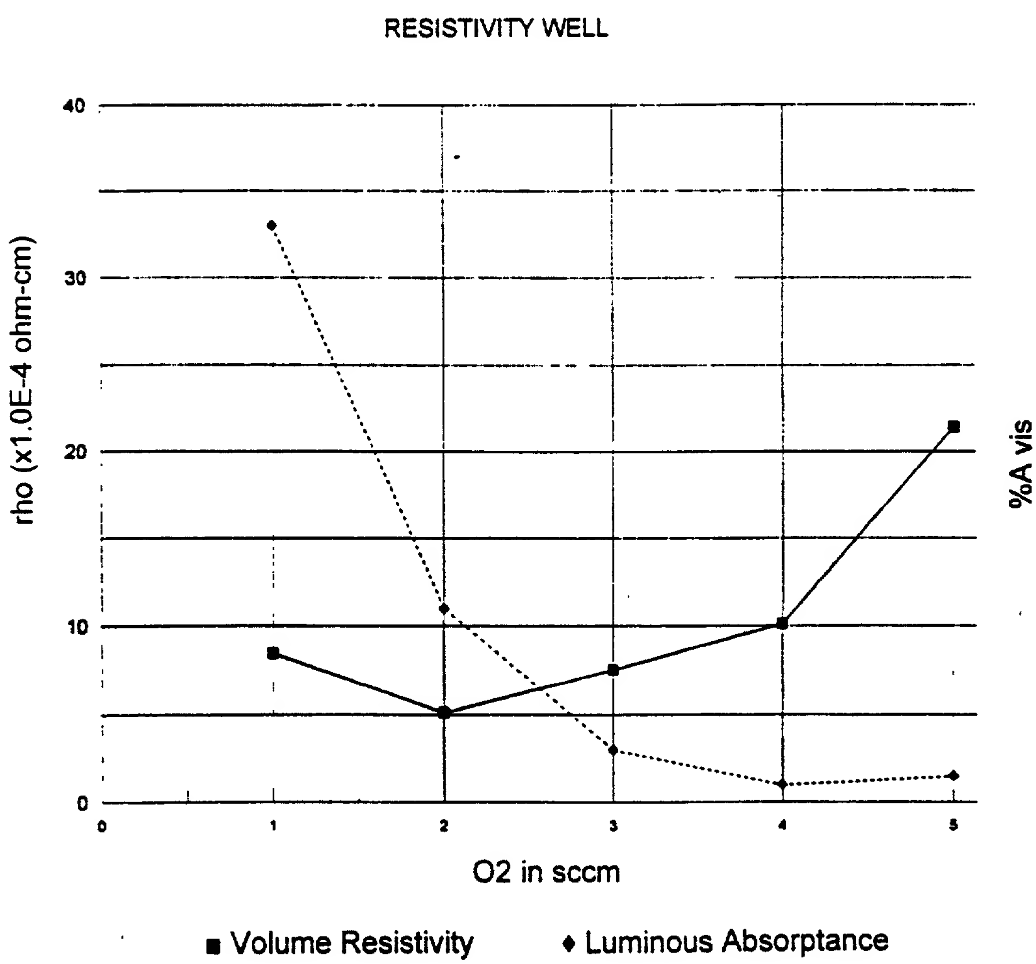
INDIUM TIN OXIDE CERAMIC TARGET

TARGET: 90 wt. % In203 / 10 wt.% SnO2 Date: 04-09-96

SUBSTRATE: ICI 725 PET

CONDITIONS: no heat
power .50 KW
speed 5.75 inch/min.
total flow 50 sccm
pressure 1.8 – 1.9 microns

O2 (sccm	1	2	3	4	5
R (ohms/square)	83.9	45.2	55.6	75.7	168.3
%T vis (Luminous)	75.5	84.6	86.5	86.3	84.5
thickness (nm, slide)	100.9	113.1	135.8	133.9	127.3
rho (x1.0E-4 ohm-cm)	8.5	5.1	7.6	10.1	21.4
%A vis (Luminous)	13.2	4.4	1.2	0.4	0.6



8

INDIUM TIN OXIDE CERAMIC TARGET

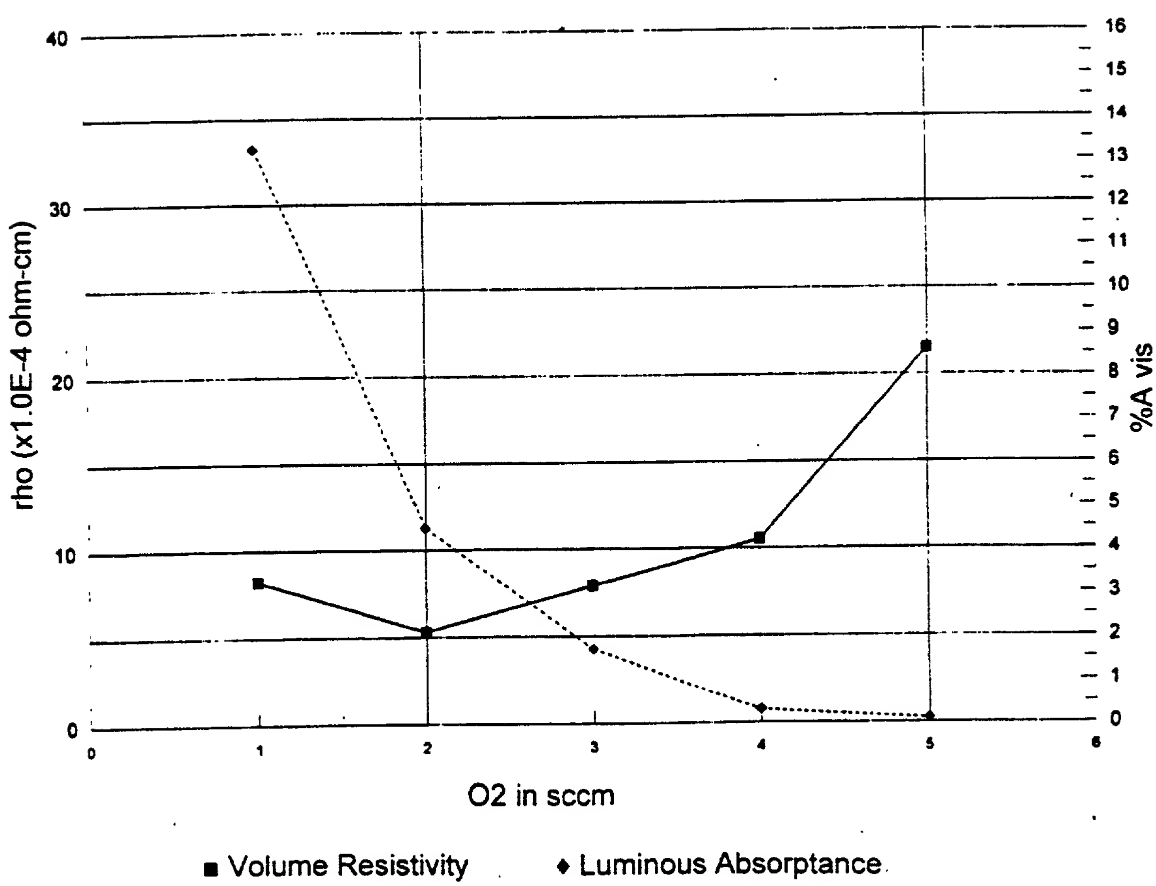
TARGET: 90 wt. % In_2O_3 / 10 wt.% SnO_2 Date: 04-09-96

SUBSTRATE: Hardcoat PET

CONDITIONS:
no heat
power .50 KW
speed 5.75 inch/min.
total flow 50 sccm
pressure 1.8 – 1.9 microns

O2 (sccm	1	2	3	4	5
R (ohms/square)	81.5	46.9	58.2	78.4	168.9
%T vis (Luminous)	74.9	84.7	87.2	87.2	85.8
thickness (nm, slide)	100.9	113.1	135.7	133.9	127.3
rho (x1.0E-4 ohm-cm)	8.2	5.3	7.9	10.5	21.5
%A vis (Luminous)	13.3	4.5	1.7	0.3	0.1

RESISTIVITY WELL



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ITO PROCESS EXAMPLES

<u>DC MAGNETRON SPUTTERING</u>

- REACTIVE PROCESS FROM 90% In / 10% Sn (WEIGHT) TARGET
- SUBSTRATE - PET (POLYETHYLENE TEREPHTHALATE) PLASTIC FILM
- TYPICAL ROLL COATER PROCESS PARAMETERS:

1. CHAMBER PRESSURE - 3.7 MICRONS (3.7 MILLITORR)
2. FLOW RATES 265 SCCM ARGON, 144 SCCM OXYGEN
3. ITO THICKNESS NEAR 100 NM
4. TARGET AREA = 75 IN^2 = 484 CM^2, SO FOR TARGET POWER OF 2000 WATTS POWER DENSITY = $\frac{4.1\ \text{WATTS}}{\text{CM}^2}$
5. DEPOSITION RATE = 6.5 $\frac{\text{NM}}{\text{SEC}}$
6. SUBSTRATE TEMPERATURE - NEAR ROOM TEMPERATURE (COOLED DRUM)

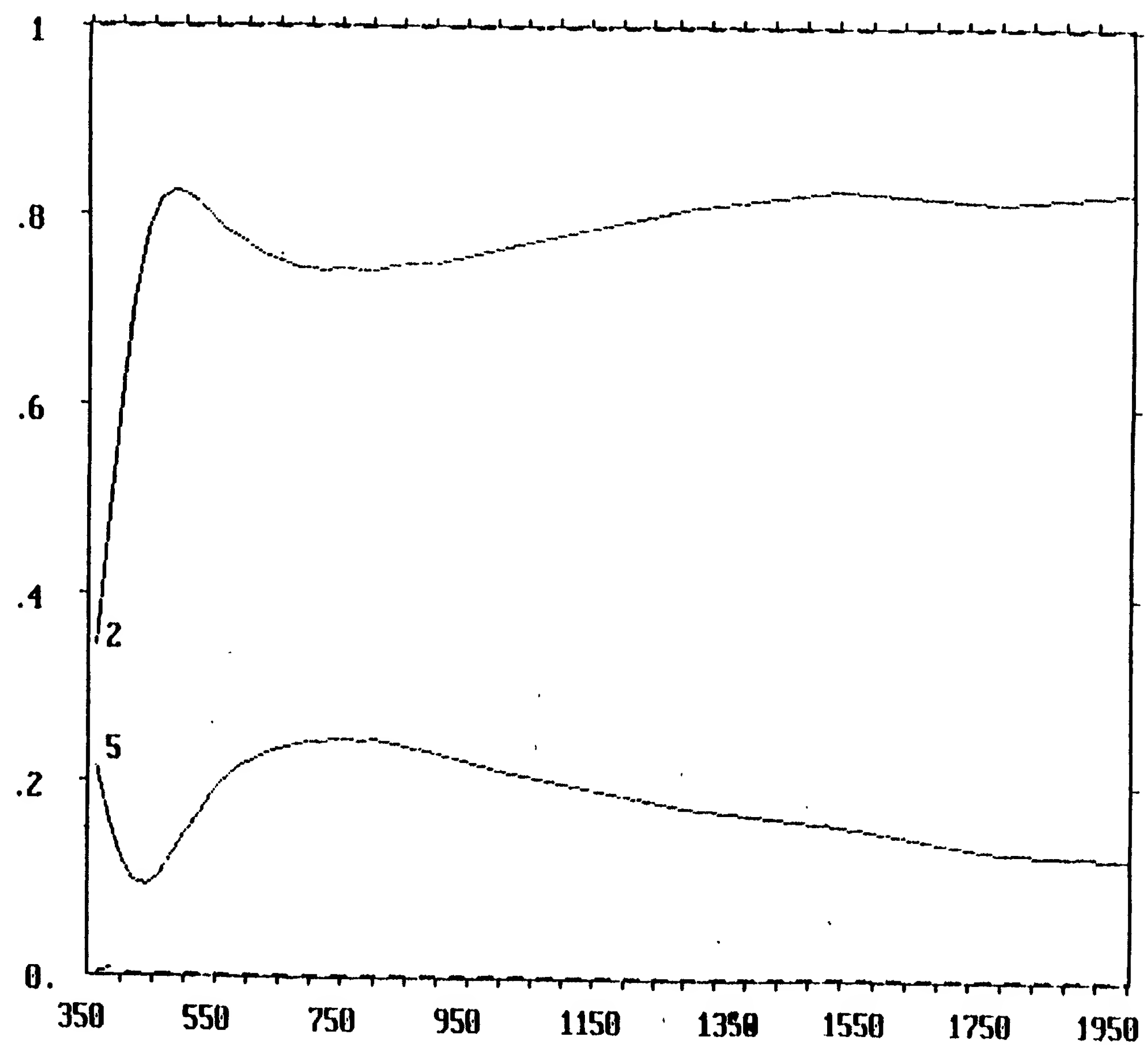
ITO PROCESS EXAMPLES

DC MAGNETRON SPUTTERING - REACTIVE PROCESS

- RESISTIVITY VERSUS OXYGEN FLOW RATE WITH CORRESPONDING OPTICAL PROPERTIES:

OHMS/SQUARE	O_2 RATE (SCCM)	LUMINOUS % T	LUMINOUS % R
74	141	78.5	18.6
192	144	79.0	19.2
232	147	80.7	16.9
370	148	81.5	16.3
555	149	82.0	15.6
1428	150	83.4	14.4
2000	155	87.4	11.2

2 for Zoom SPECTRA VS WAVELENGTH PASS 1 GLOW METERS: 15.7



Tvi 79.0 TW@ 492. TW@ 0.
Rvi 19.2 RW@ 438. RW@ 753.

3

ITO PROCESS EXAMPLES

DC MAGNETRON SPUTTERING

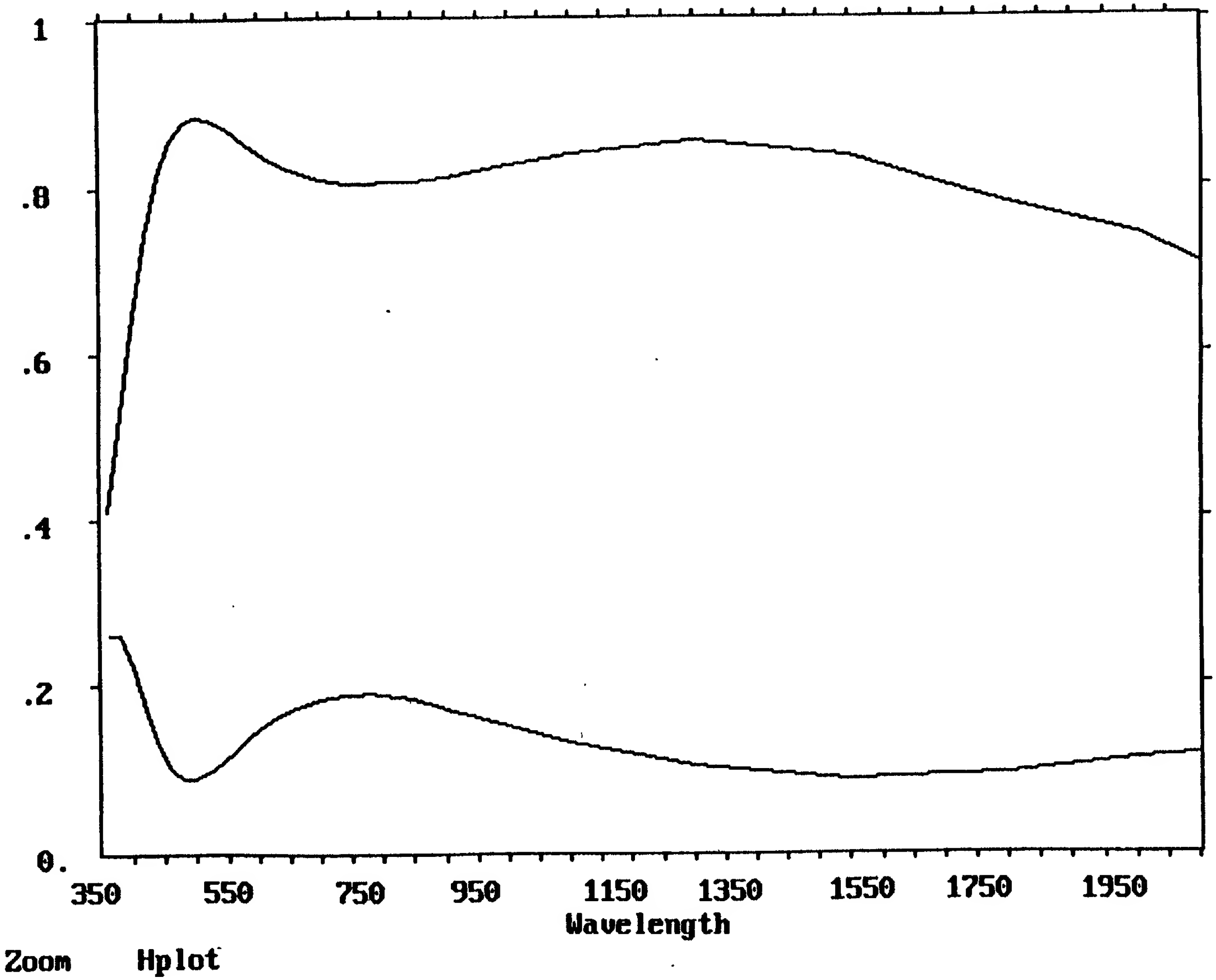
- SEMIREACTIVE PROCESS FROM 90% In_2O_3 / 10% SnO_2 (WEIGHT) CERAMIC TARGET

- SUBSTRATES - PET FILM AND GLASS SLIDES

- TYPICAL IN-LINE COATER PROCESS PARAMETERS:

1. CHAMBER PRESSURE - 2 MICRON (2 MILLITORR)
2. FLOW RATES - 45 - 49 SCCM ARGON 1 - 5 SCCM OXYGEN
3. ITO THICKNESS NEAR 130 NM
4. TARGET AREA = 48 IN^2 = 310 CM^2 SO FOR TARGET POWER OF 500 WATTS POWER DENSITY = 1.6 $\frac{WATTS}{CM^2}$
5. DEPOSITION RATE = $\frac{3\ NM}{SEC}$
6. SUBSTRATE TEMPERATURE - NEAR ROOM TEMPERATURE

Set: 5 : File: B: /OPTICAL/DTA2.QPE : ITO/90/10/PET/02/BHT/55.6/OHMS/SQ/1358A/T



IO PROCESS EXAMPLE

<u>THERMAL EVAPORATION</u>

- REACTIVE PROCESS FROM In METAL

- SUBSTRATES - GLASS AND OTHER TEMPERATURE TOLERANT MATERIALS

- TYPICAL BELL JAR COATER PROCESS PARAMETERS:

1. CHAMBER PRESSURE - 1 TO 3 MILLITORR
2. FLOW RATE - MAINTAIN OXYGEN PRESSURE
3. IO THICKNESS - 100 NM TO 143 NM
4. RATE - 0.1 $\frac{NM}{SEC}$
5. SUBSTRATE TEMPERATURE - 230 °C

IO PROCESS EXAMPLE

THERMAL EVAPORATION

- RESISTIVITY VERSUS OXYGEN PRESSURE:

OHMS/SQUARE	THICKNESS (NM)	RHO (MILLIOHMS-CM)	O_2 PRESSURE (MILLITORR)
27.0	142.0	0.38	1.0
32.8	105.0	0.34	2.0
54.8	99.7	0.55	3.0

IO PROCESS EXAMPLE

THERMAL EVAPORATION

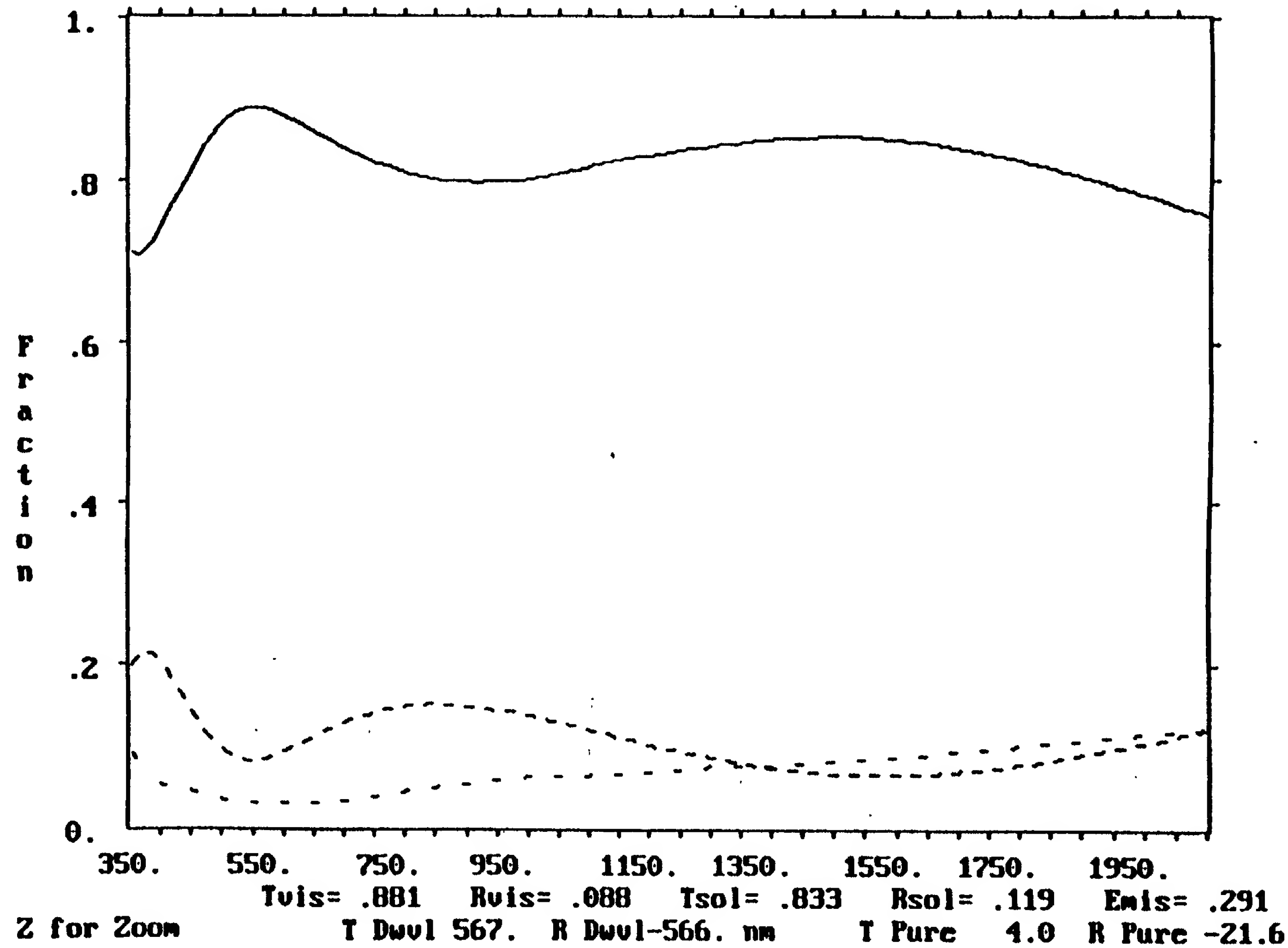
- OPTICAL PERFORMANCE:

LUMINOUS TRANSMITTANCE	= 88.1%
LUMINOUS REFLECTANCE	= 8.8%
LUMINOUS ABSORPTANCE (AND SCATTERING)	= 3.1%
REFRACTIVE INDEX AT 550 NM	= 1.91
EXTINCTION COEFFICIENT AT 550 NM	= 8.2×10^{-3}

- ELECTRICAL PERFORMANCE:

SURFACE RESISTIVITY	= 27.0 OHMS/SQUARE
THICKNESS	= 142.3 NM
RESISTIVITY	= 3.8×10^{-4} OHMS - CM
ELECTRON DENSITY	= 9.2×10^{20} CM^{-3}
MOBILITY	= 18 $\frac{CM^2}{\text{VOLT SEC}}$

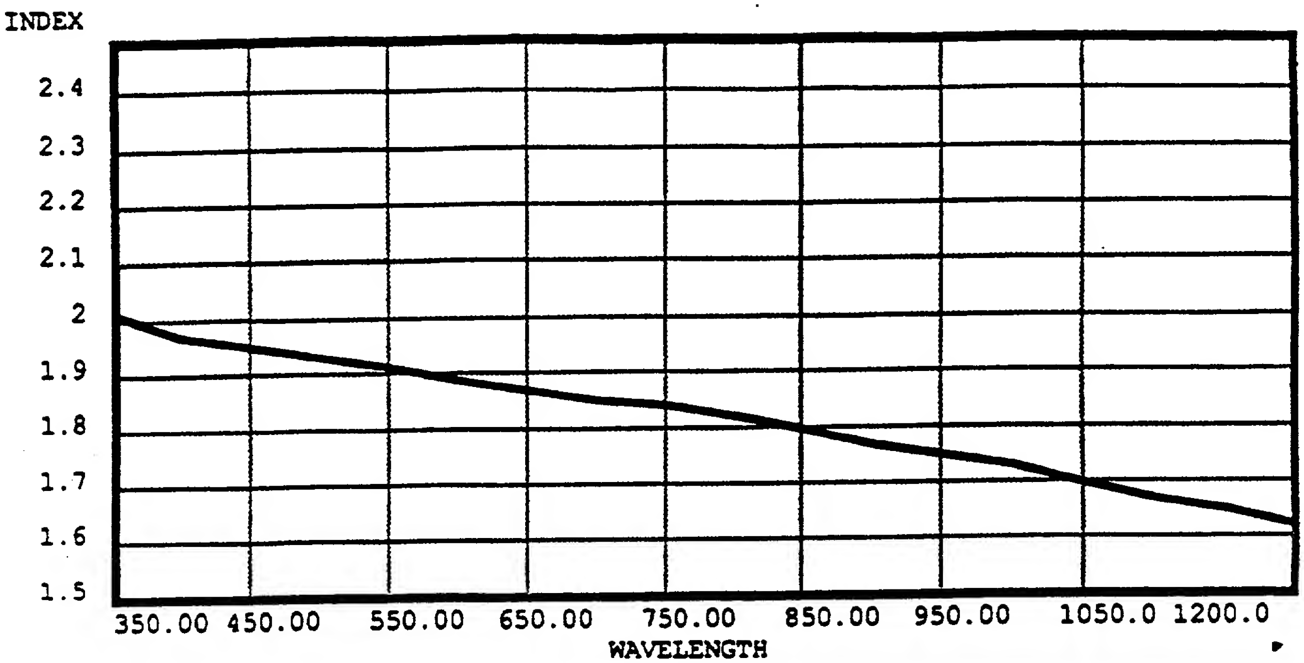
IO PROCESS EXAMPLE

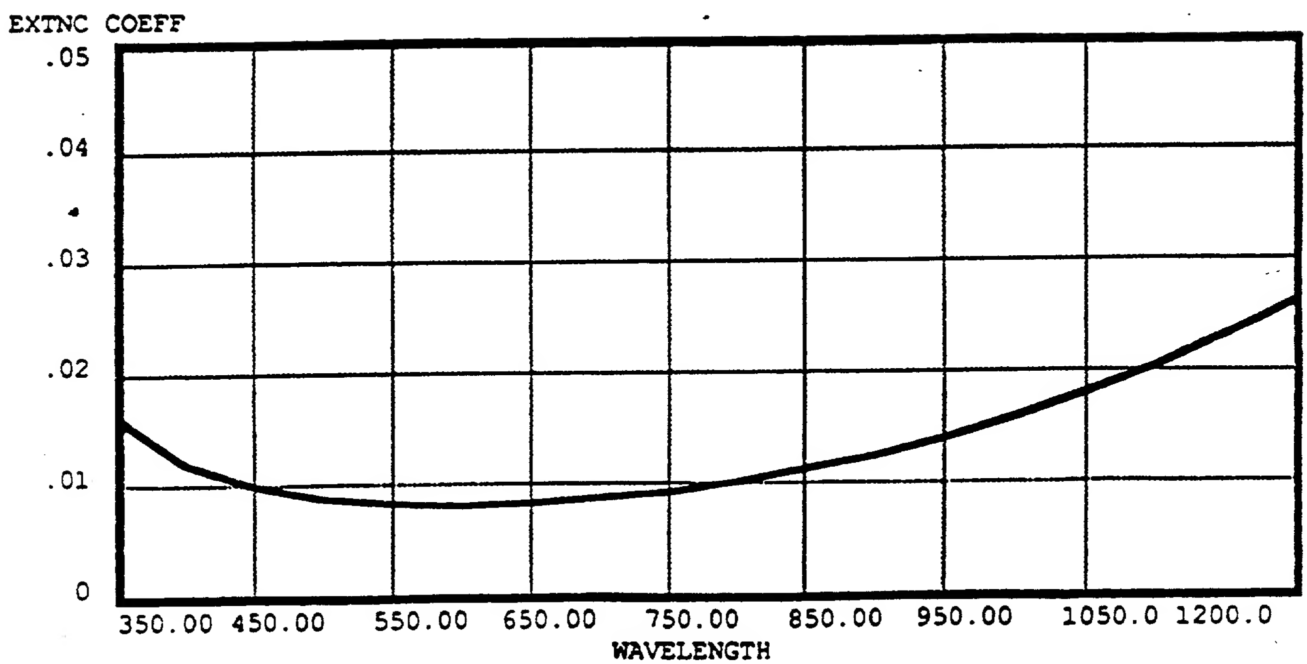


Thermal Evaporated Indium Oxide Coating on Glass, 27 Ohms/Square

Transmittance – upper trace, Reflectance – middle trace, Absorptance – lower trace

IO PROCESS EXAMPLE





Optical Constant for Evaporated Indium Oxide Coating on Glass 1 mtorr O_2, 27 Ohms/Square

(From C. I. Bright, 36th SVC Tech. Con. Proc., (1993) 63 – 67)

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ZrN PROCESS EXAMPLE

DC MAGNETRON SPUTTERING

- REACTIVE PROCESS FROM Zr METAL TARGET
- SUBSTRATE-CORNING 7059 GLASS AND SILCON WAFERS
- TYPICAL IN-LINE COATER PROCESS PARAMETERS

1. CHAMBER PRESSURE = 0.2 – 0.3 Pa
2. FLOW RATES = 100 sccm ARGON, 15 – 25 sccm NITROGEN
3. ZrN THICKNESS ~ 18 – 390 nm
4. TARGET POWER = 1400 - 2400 WATTS
5. TARGET/SUBSTRATE DISTANCE = 120 mm
6. DEPOSITION RATE = 6 nm/sec
7. SUBSTRATE TEMPERATURE = 150 °C, 300 °C

(Data from M Veszelei et al, Optical Constants and Drude Analysis of Sputtered ZrN Films, Applied Optics, 33,10 1994)

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ZrN PROCESS EXAMPLE

DC MAGNETRON SPUTTERING

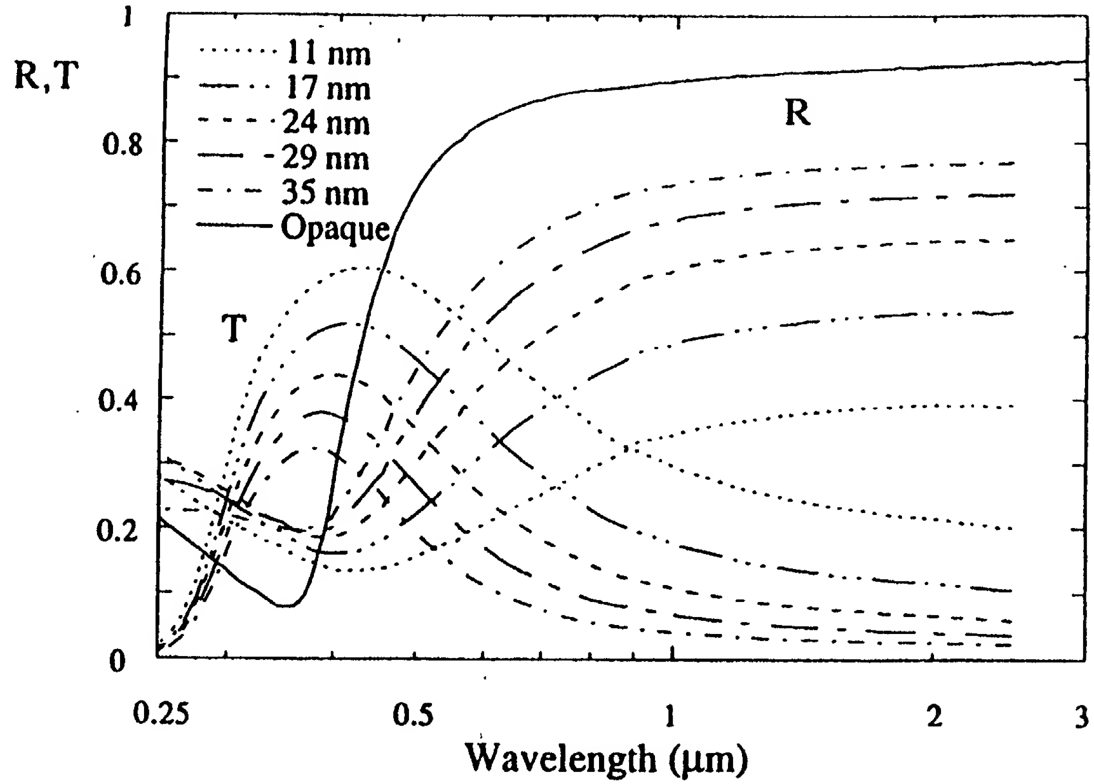
- REFLECTANCE AS A FUNCTION OF NITROGEN FLOW RATE

N_2 FLOW RATE (SCCM)	REFLECTANCE (%) MINIMUM	REFLECTANCE (%) AT 2 um	REFLECTANCE (%) AT 10 um
15	18% (305 nm)	77%	86%
*18	*15% (~420 nm)	*86%	*93%
20	8% (355 nm)	91%	94%
25	9% (355 nm)	90%	94%

(Data From M. Veszelei et al, A.O., 33 10, 1994 and *Data From A. Spencer et al, Solar Energy Material, 18,1988)

ZrN PROCESS EXAMPLE

DC MAGNETRON SPUTTERING



Reflectance and Transmittance for Various Thickness of ZrN Films.
(From M. Veszelei et al, Optical Characterization of Sputtered Semi-Transparent ZiN Films, Optical Materials 2, 1993)

TiN PROCESS EXAMPLE

RF MAGNETRON SPUTTERING

- REACTIVE PROCESS FROM Ti METAL TARGET
- SUBSTRATE-CORNING 7059 BOROSILICATE GLASS
- R&D COATER

8. CHAMBER PRESSURE = 0.67 Pa
9. GAS MIXTURE = ARGON WITH 8% NITROGEN
10. THICKNESSES = 4 – 76 nm
11. TARGET POWER = 100 WATTS
12. DEPOSITION RATE = 10.6 nm/min
13. SUBSTRATE TEMPERATURE = 400 °C

(Data from M. Kawamura et al, Characterization of Thin, Transparent and Conductive TiN Films, JVST A, 16 (1) 1998)

TiN PROCESS EXAMPLE

RF MAGNETRON SPUTTERING

- ELECTRICAL AND OPTICAL PROPERTIES OF TiN THIN FILMS

Thickness (nm)	Sheet resistance (Ω/□)	Resisticity (μΩ cm)	T*max* (%)
4.2	173	73	79
5.3	123	65	76
11	43	46	64
21	19	40	47
52	5.7	30	26

(From M. Kawamura et al, Characterization of TiN Films, JVST A 16 (1) 1998)

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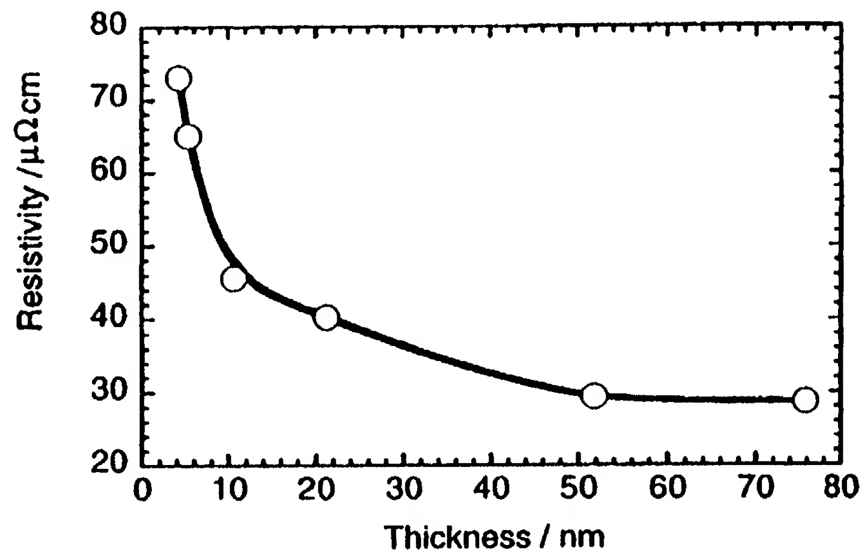
TiN PROCESS EXAMPLE

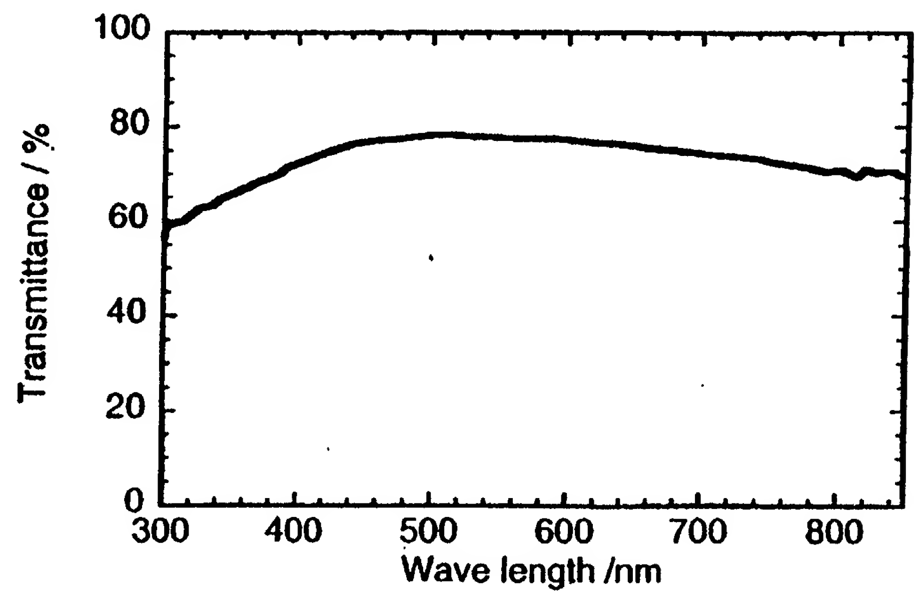
RF MAGNETRON SPUTTERING



The Resistivity (ρ) Change With Film Thickness of TiN Films.
(From M. Kawamura et al, Characterization of TiN Films, JVST A 16 (1) 1998)

TiN PROCESS EXAMPLE

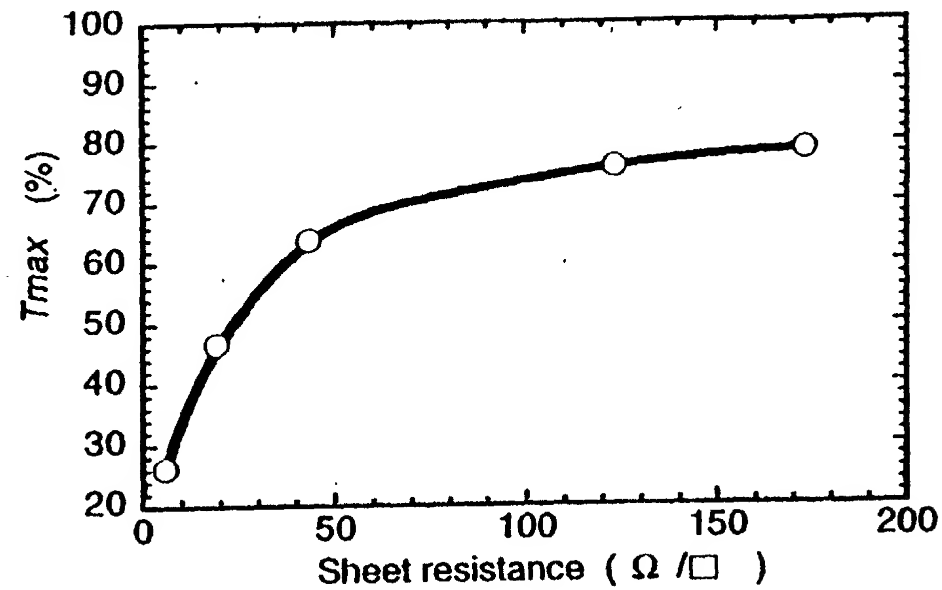
RF MAGNETRON SPUTTERING



Transmission of TiN Film (d=4.2 nm) (Glass Substrate Removed).
(From M. Kawamura et al, characterization of TiN Films, JVST A 16 (1) 1998)

TiN PROCESS EXAMPLE

RF MAGNETRON SPUTTERING



Relationship Between Sheet Resistance and Maximum Transmission (at ~500 nm) of TiN Films.

(From M. Kawamura et al, Characterization of TiN Films, JVST A 16 (1) 1998)

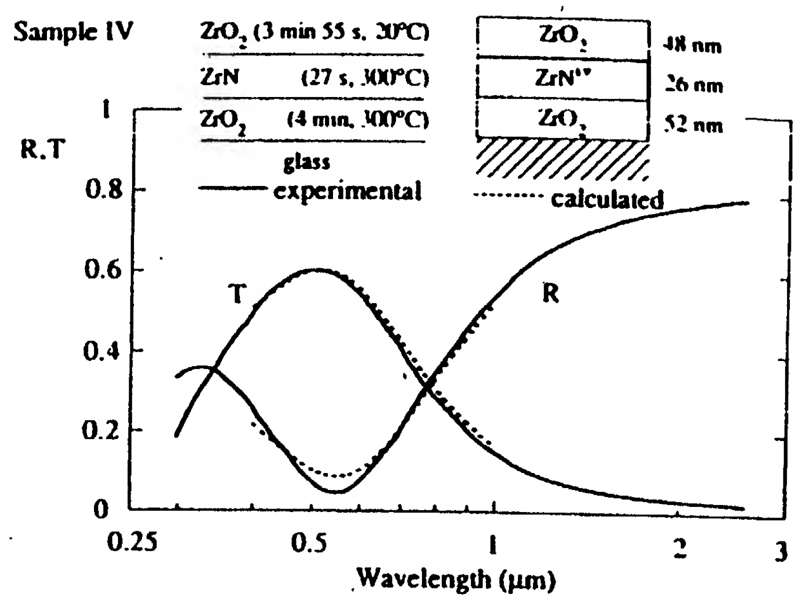
KEY COATING PARAMETERS BY APPLICATION FUNCTION

Parameter	Transparent Electrodes	EMI Shield	Heater	Antistatic	Heat Mirror	AR
Resistance (Ohms)			X	X		
Surface Resistivity (Ohms/Square)	X	X				
Visible Transmittance	X	X	X	X	X	X
Visible Reflectance						X
Infrared Reflectance					X	

APPLICATION EXAMPLES

HEAT MIRROR

- OPTICALLY ENHANCED ZrN

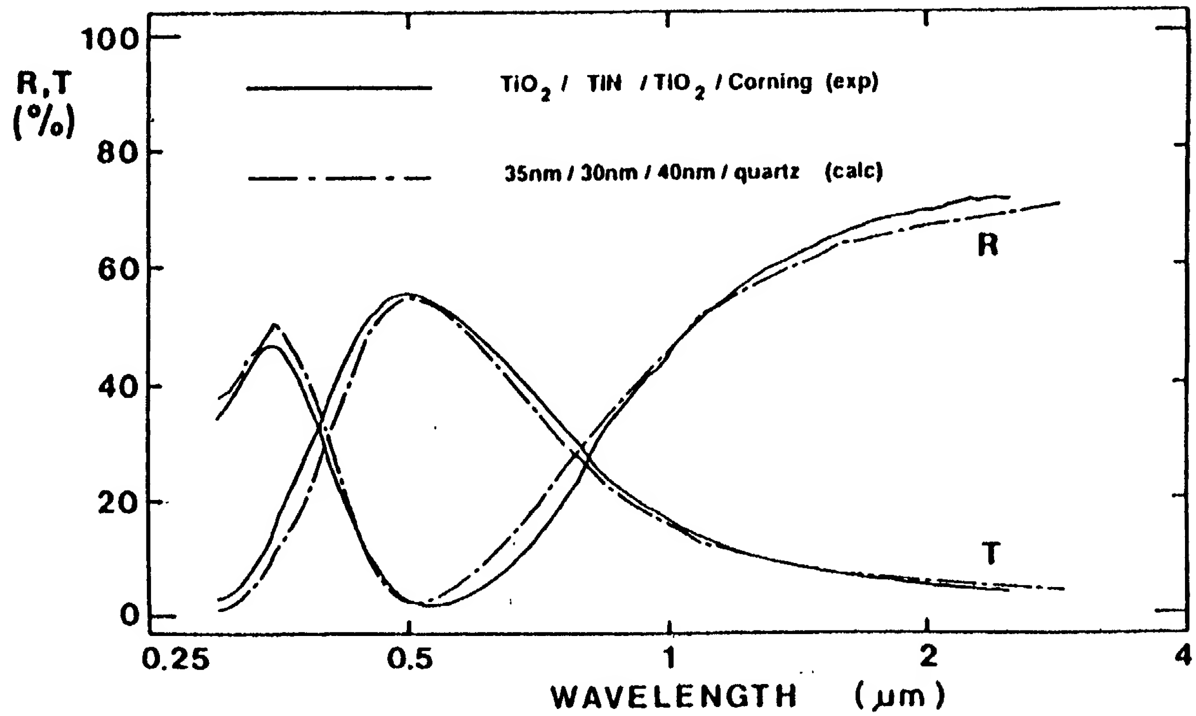


Calculated and Measured Reflectance and Transmittance for $ZrO_2/ZrN/ZrO_2$.
(From K. Andersson et al, ZrN Based Transparent Heat Mirror Coatings, Solar Energy Mat. 32, 1994)

APPLICATION EXAMPLES

HEAT MIRROR

- OPTICALLY ENHANCED TiN



Calculated and Measured Reflectance and Transmittance for $TiO_2/TiN/TiO_2$.
(From Y. Claesson et al, Characterization of TiN-Based Solar Control Coatings, Solar Energy Mat. 20, 1990)

1C

MATCHING APPLICATION REQUIREMENTS

RESISTIVITY ANTI – ICING HEATER FOR TV AND LASER WINDOW

REQUIREMENTS

- Power Dissipation Of 1.5 Watts/in^2 From 28 Volt Source
- Coated Window Transmittance of

  T visible > 84% From 525 nm 625 nm
  T average > 83% Between 700 nm 900 nm
  T laser > 82% At 1070nm

- Laser Damage Resistant
- Durability to MIL-C-48497

MATCHING APPLICATION REQUIREMENTS

- APPLICATION TYPE: Resistive Heater

- TRADEOFF PRIORITIES:

  1. Electrical Performance (resistance)
  2. Optical Performance
  3. Laser Damage Resistance
  4. Durability
  5. Cost

MATCHING APPLICATION REQUIREMENTS

- Coating Surface Resistivities Between 10.6 And 14.2 Ohms/Square Yields Correct Resistance For Proper Heating
- Two Layer ITO/SIO_2 Coating Design Meets Optical Requirements
- Design Adjusted For Electric Field Control At Interfaces
- Durability Met By Materials Choice And Deposition Process

MATCHING APPLICATION REQUIREMENTS

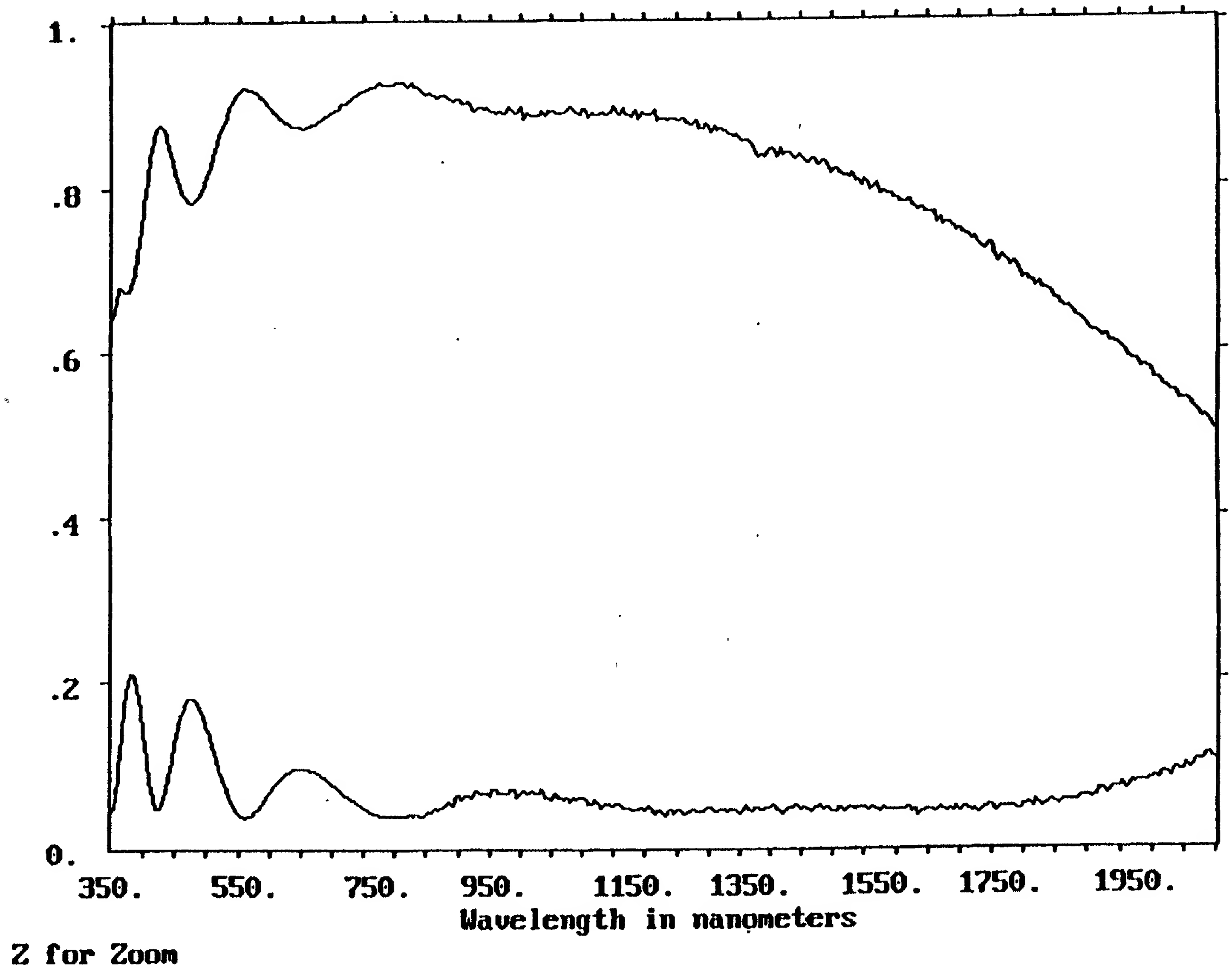
MEASURED TCO PERFORMANCE

- Heater Resistance = 7.9 Ohms (11.3 OHMs/Square)
- Window Transmittance

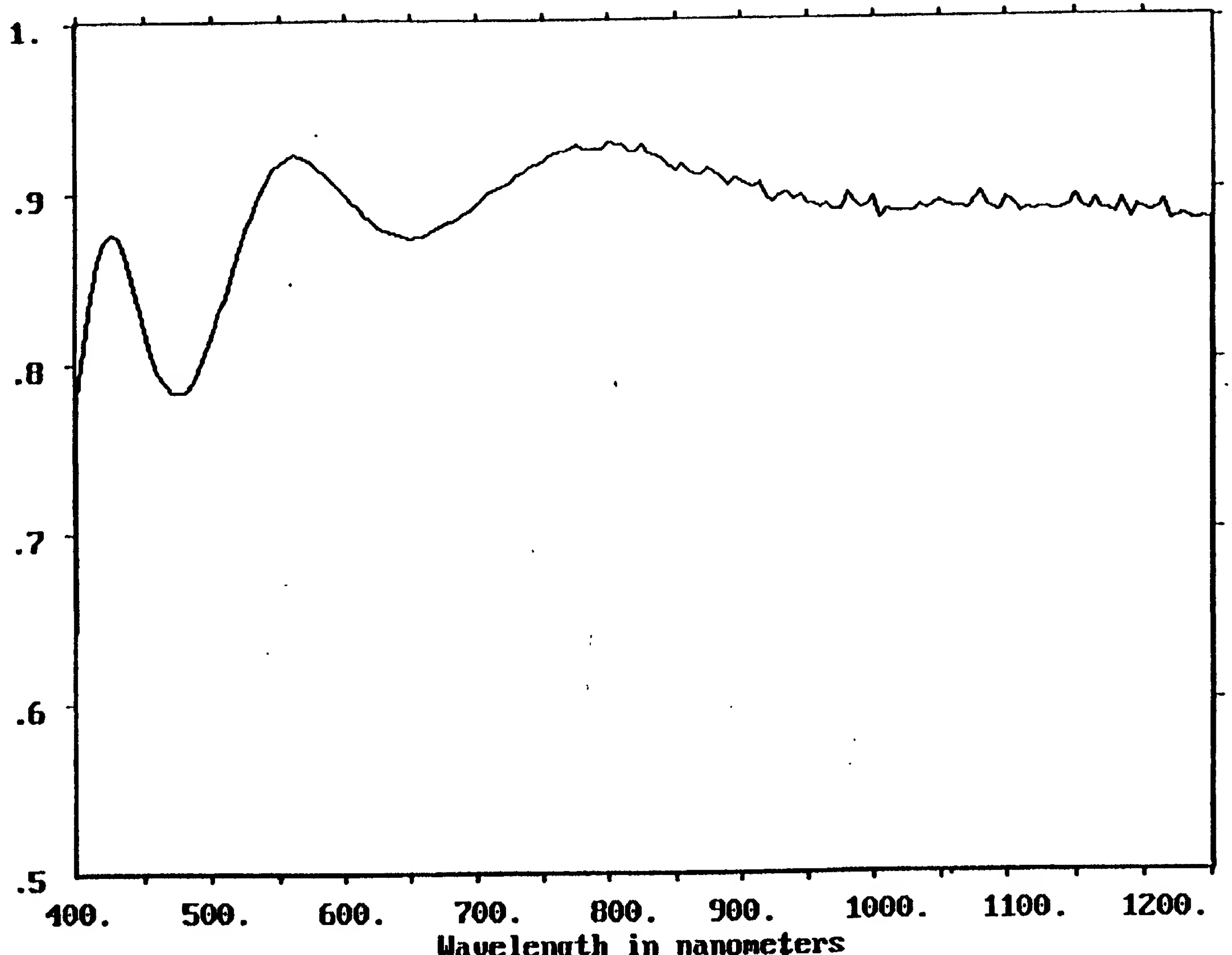
  T visible 525nm – 625nm = 88%
  T average 700nm – 910nm = 92%
  T laser 1070nm = 89%

- Passed Laser Damage Testing At 22.5 to 36.0 MW/cm^2
- Passed Durability Tests Of MIL-C-48497

RESISTIVITY ANTI-ICING HEATER FOR TV AND LASER WINDOW



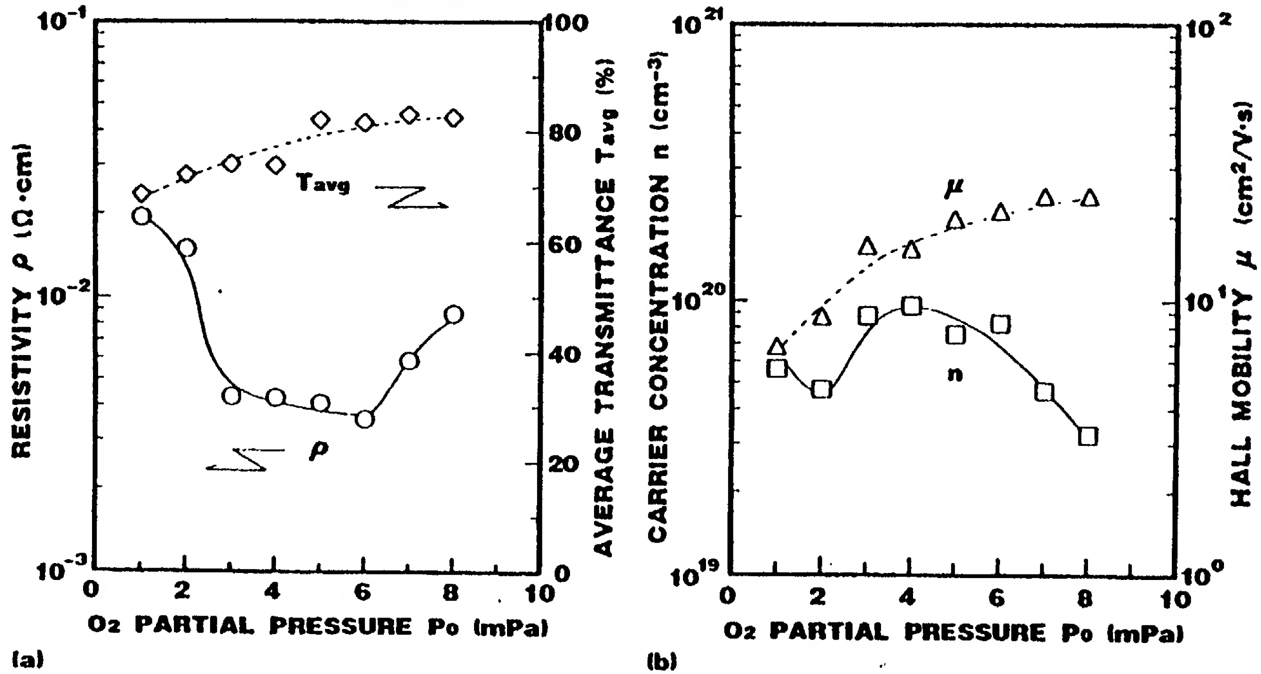
RESISTIVITY ANTI-ICING HEATER FOR TV AND LASER WINDOW



Z for Zoom

ADVANCED TOPICS

NEW TCO MATERIALS

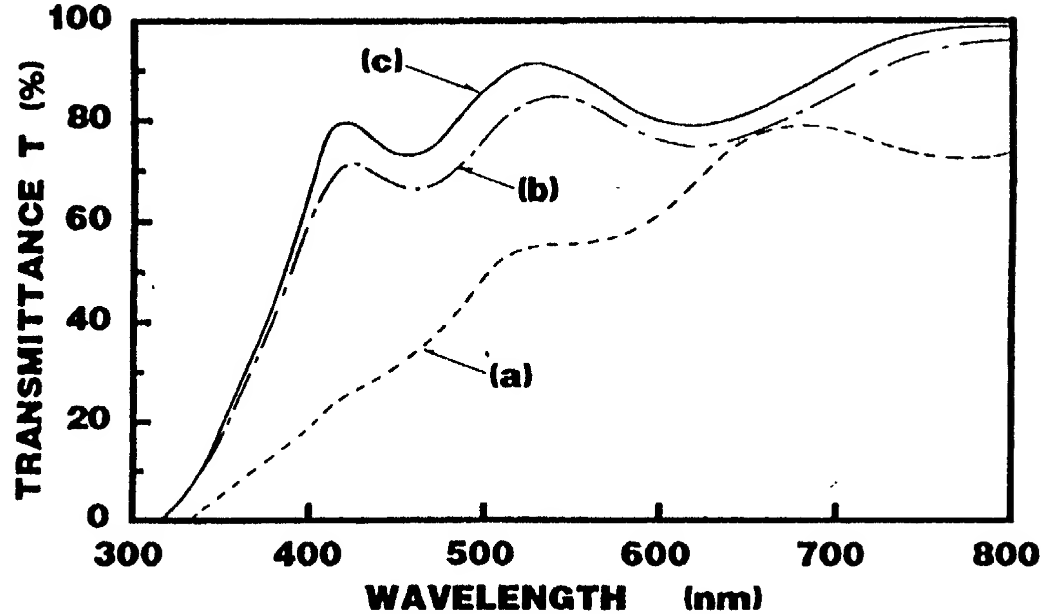


(a) Resistivity (o) and Average Transmittance in the Visible Range (◊), (b) Hall Mobility (Δ) and Carrier Concentration (□) as Functions of the Oxygen Partial Pressure for Zinc Stannate Films Prepared at RT (~140°C).

(From T. Minami et al, Preparation of Transparent Zinc Stannate Conducting Films, JVST A, 13, 3 1995)

ADVANCED TOPICS

NEW TCO MATERIALS

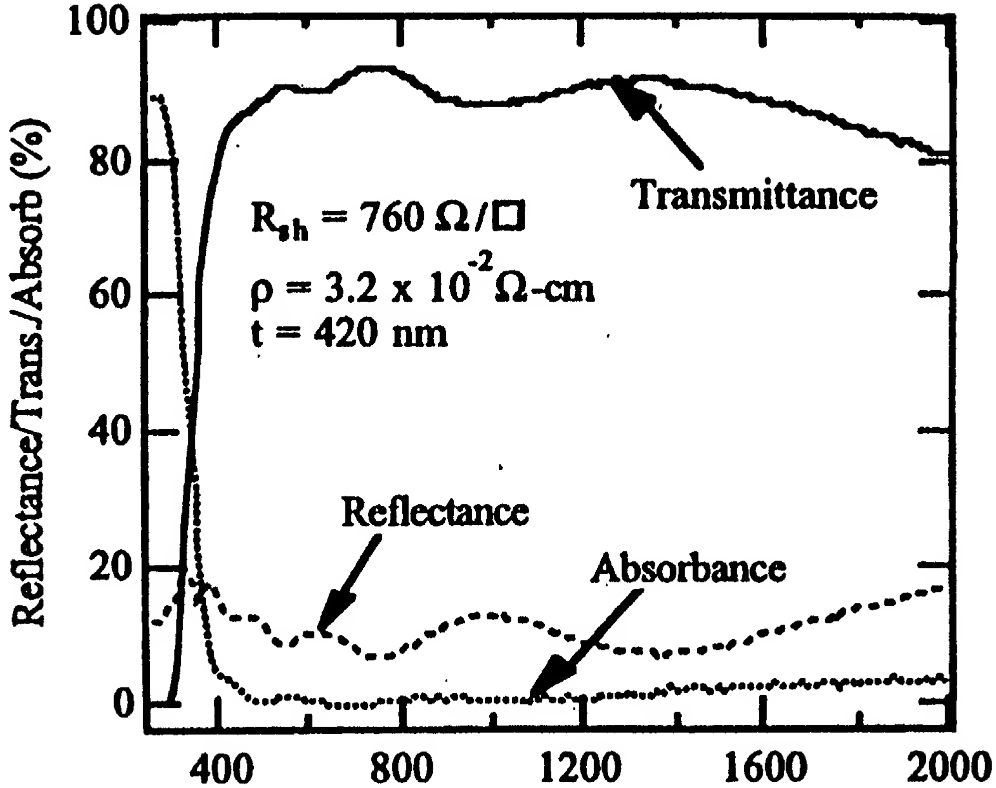


Transmission Spectra for Zinc Stannate Films Deposited with Oxygen Partial Pressures of 0 Pa [curve (a), Film Thickness of 470nm], 2 mPa [curve (b), 310 nm] and 5 mPa [curve (c), 300 nm].

(From T. Minami et al, Properties of Transparent Zinc-Stannate Conducting Films, JVST A, 13, 3 1995)

ADVANCED TOPICS

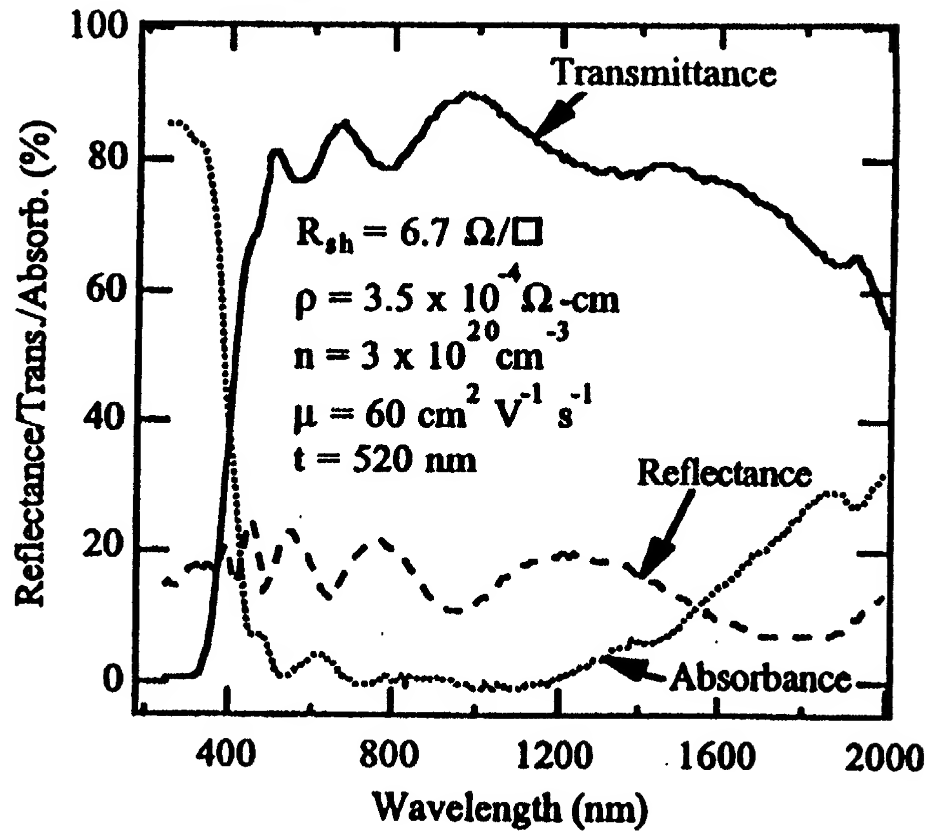
NEW TCO MATERIALS



Transmittance, Reflectance, and Absorbance for a Zn_2SnO_4 Film.
(From X. Wu et al, Properties of Transparent Conducting Cd_2SnO_4 and Zn_2SnO_4, 39th SVC, 1996)

ADVANCED TOPICS

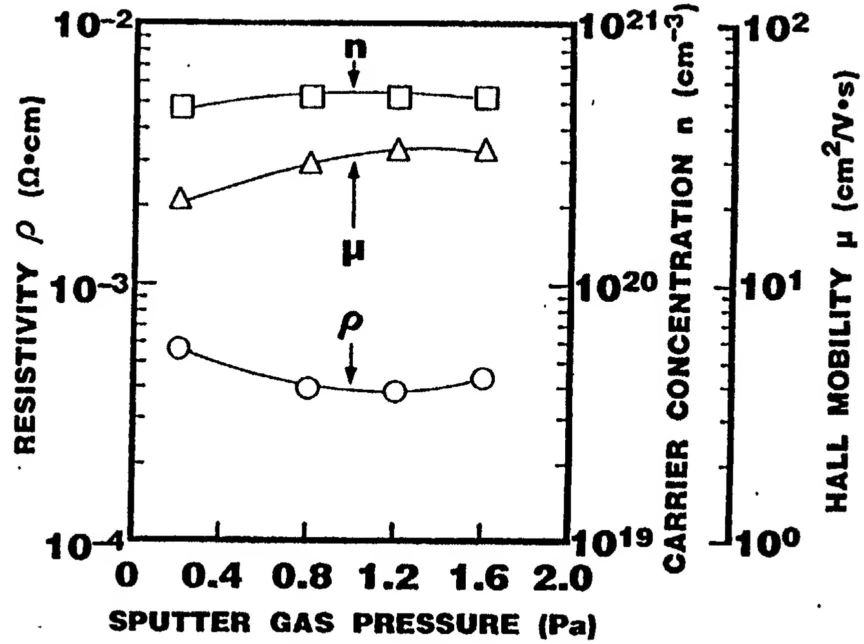
NEW TCO MATERIALS



Transmittance, Reflectance, and Absorbance for a Cd_2SnO_4 Film.
(From X. Wu et al, Properties of Transparent Conducting Cd_2SnO_4 and Zn_2SnO_4, 39th SVC, 1996)

ADVANCED TOPICS

NEW TCO MATERIALS

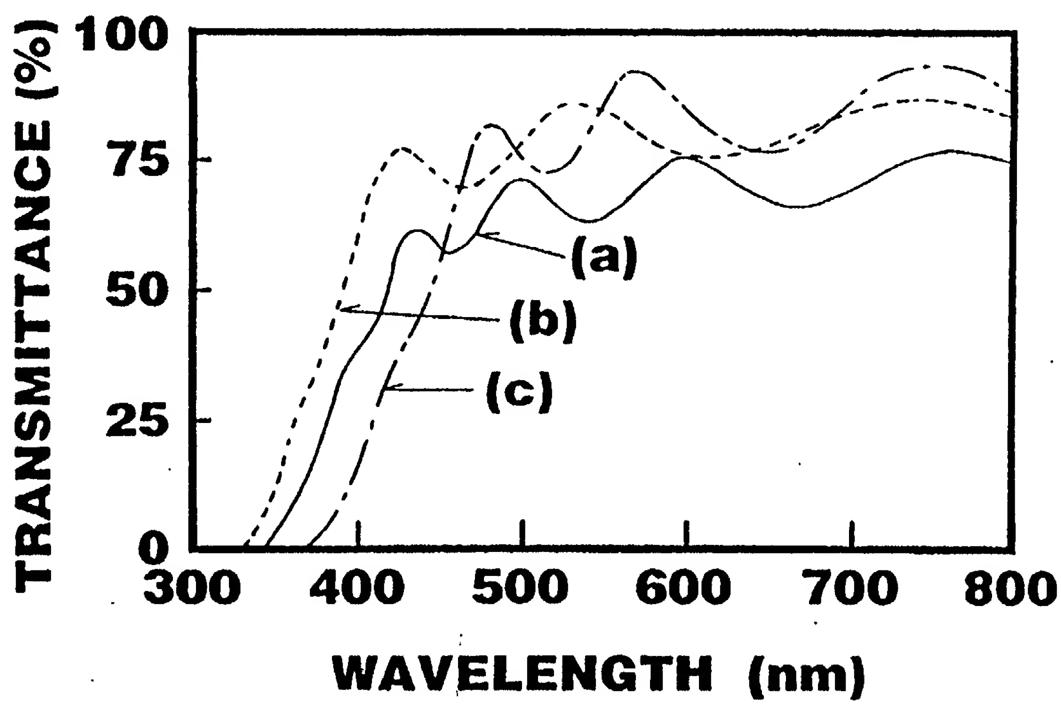


Resistivity (o), Carrier Concentration (□) and Hall Mobility (Δ) as a Function of Sputter Gas Pressure for $Zn_2In_2O_5$ Films (Substrate ~140°C).

(From T. Minami et al, New Transparent Conducting $Zn_2In_2O_5$ Thin Films, ICMCTF, 1995)

ADVANCED TOPICS

NEW TCO MATERIALS

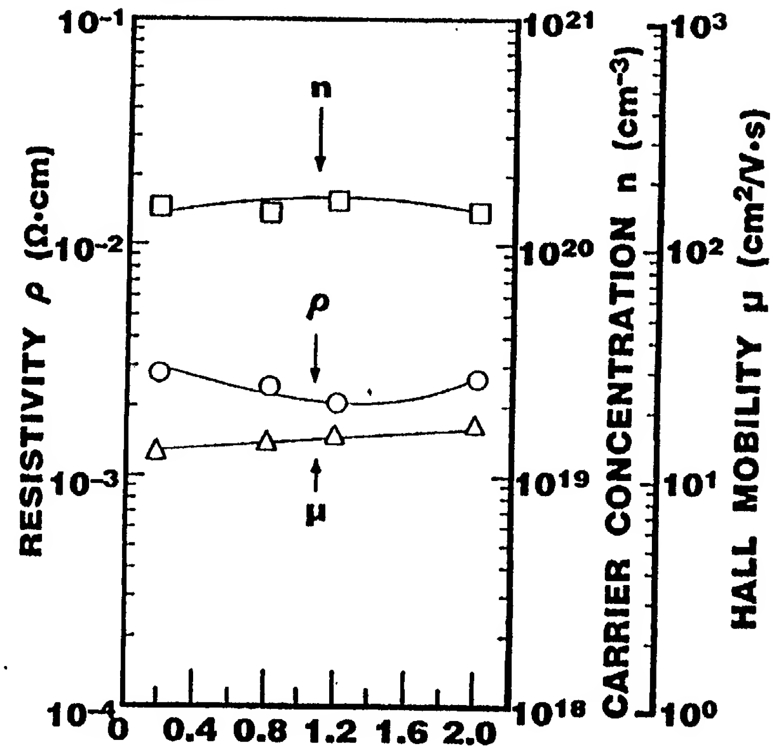


Optical Transmission for $Zn_2In_2O_5$ Films Prepared with Different Conditions; (a) RT Substrate (~140°C), Ar only, (b) 350°C Substrate, Ar only, (c) RT Substrate (~140°C), Ar 20% + O_2.

(From T. Minami et al, New Transparent Conducting $Zn_2In_2O_5$ Thin Films, ICMCTF, 1995)

ADVANCED TOPICS

NEW TCO MATERIALS

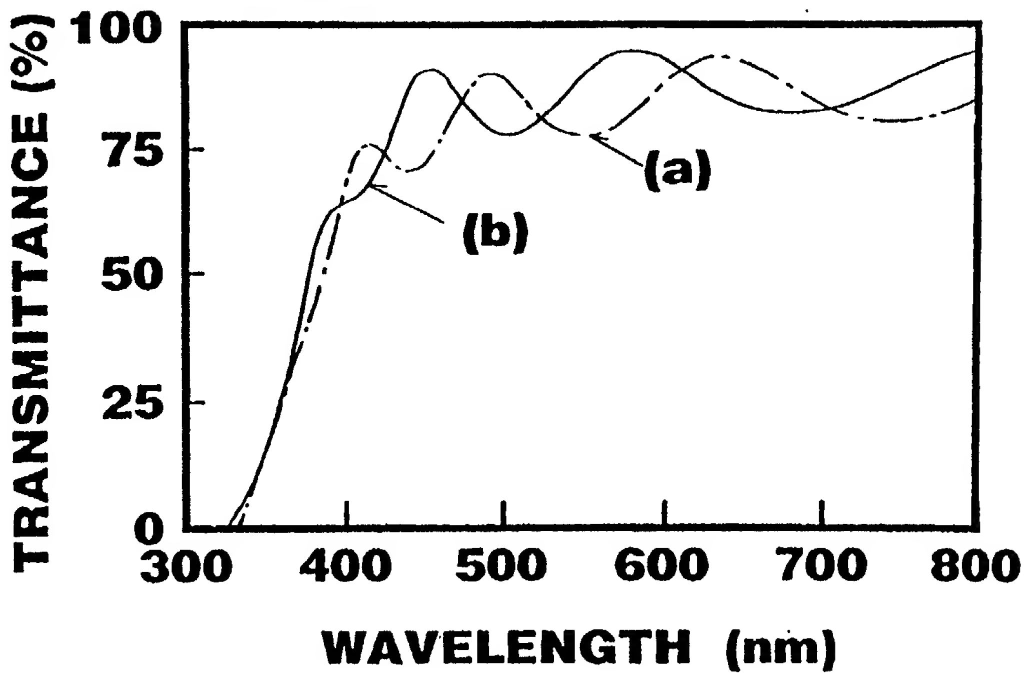


Resistivity (o), Carrier Concentration (□) and Hall Mobility (Δ) as a Function of Sputter Gas Pressure for $MgIn_2O_4$ Films (RT Substrate ~140°C).

(From T. Minami et al, New Transparent Conducting $Zn_2In_2O_5$ Thin Films, ICMCTF, 1995)

ADVANCED TOPICS

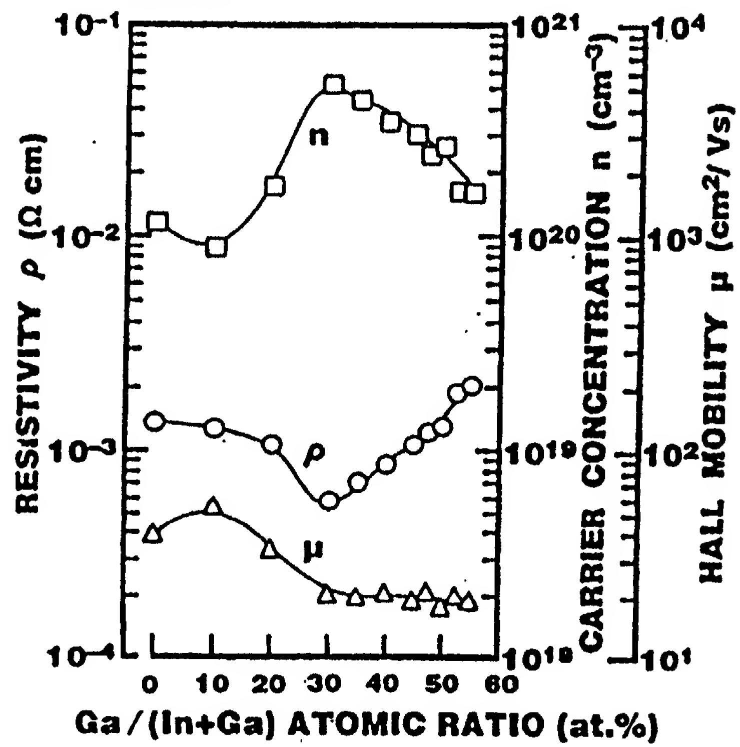
NEW TCO MATERIALS



Optical Transmission of $MgIn_2O_4$ Films [Ar pressure (a) 0.8 Pa, (b) 1.2 Pa].
(From T. Minami et al, New Transparent Conducting $MgIn_2O_4$ Thin Films, ICMCTF, 1995)

ADVANCED TOPICS

NEW TCO MATERIALS

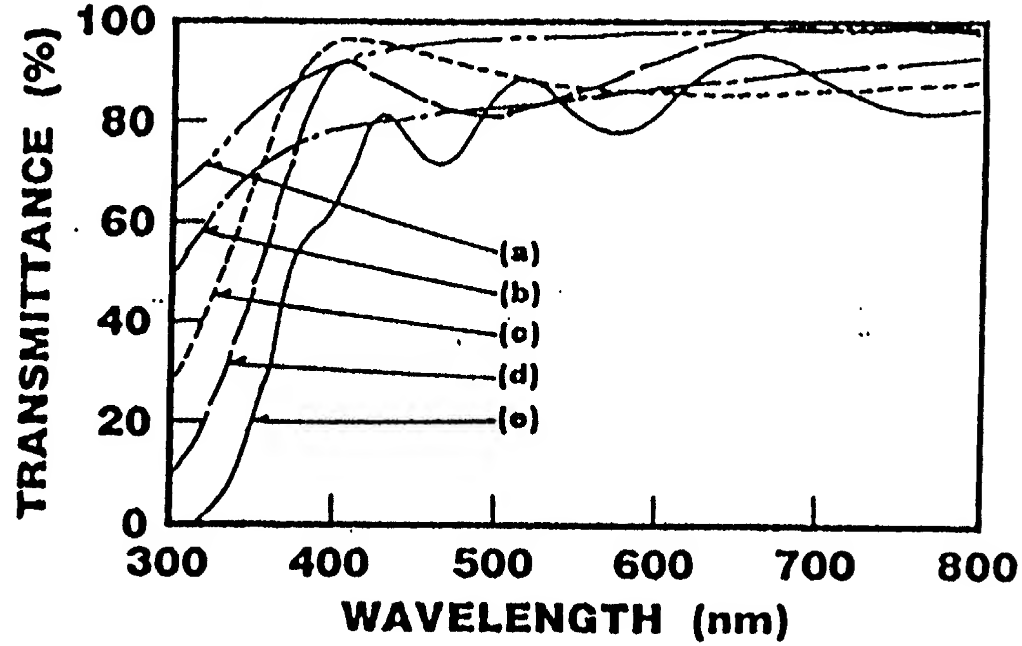


Resistivity (o), Carrier Concentration (□) and Hall Mobility (Δ) as Functions of Ga Content for Ga_2O_3-In_2O_3 Films Prepared at RT (~180ºC).

(From T. Minami et al, Preparation of Highly Transparent Films, JVST A, 15, 3 1997)

ADVANCED TOPICS

NEW TCO MATERIALS



Transmittance of $(Ga,In)_2O_3$ Films Prepared at RT (~180ºC) With Ga Content of 50 at. % and Thickness of (a) 20, (b) 55, (c) 100, (d) 185 and (e) 500 nm.

(From T. Minami et al, Preparation of Highly Transparent Films, JVST A, 15, 3 1997)

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ADVANCED TOPICS

EXCIMER LASER (XeCl @ 308 nm) ABLATION

- ELECTRICAL AND OPTICAL PROPERTIES OF ZnO FILMS PREPARED AT SUBSTRATE TEMPERATURE OF 300°C.

	Al-doped ZnO	Ga-doped ZnO
Resitivity ($\Omega \bullet$ cm)	$1.4X10^{-4}$	$2.7x10^{-4}$
Hall mobility (cm2/V • s)	45	18
Carrier concentration (cm^{-3})	$9.9x10^{20}$	$1.3x10^{21}$
Transmittance (%)	90	90
Film thickness (nm)	150	230
Dopant in target (wt%)	1.0	7.0

(From K Imaede et al, Highly Conductive and Transparent ZnO :Al Thin Films, Presented at 43rd AVS, 1996)

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SECTION III: MAJOR DEPOSITION METHODS FOR TCC

1. I. Maissel and R. Glang, Editors, *Handbook of Thin Film Technology*, McGraw-Hill Book Co., New York (1970)

SECTION V: DEVELOPING A TCO DEPOSITION PROCESS

SECTION IV: IMPORTANT PROCESS PARAMETER FOR TRANSPARENT CONDUCTIVE OXIDES (TCO)

SECTION V: DEVELOPING A TCO DEPOSITION PROCESS

SECTION VI: TCO PROCESS EXAMPLES AND ASSOCIATED COATING PROPERTIES

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SECTION VII: STRATEGY FOR DEVELOPING A TCC TO MEET SPECIFIC APPLICATION REQUIREMENTS

SECTION VIII: APPLICATION EXAMPLES

SECTION IX: SPECIFING AND SELECTING COMMERCIALLY AVAILABLE TCC

SECTION X: ADVANCED TOPICS

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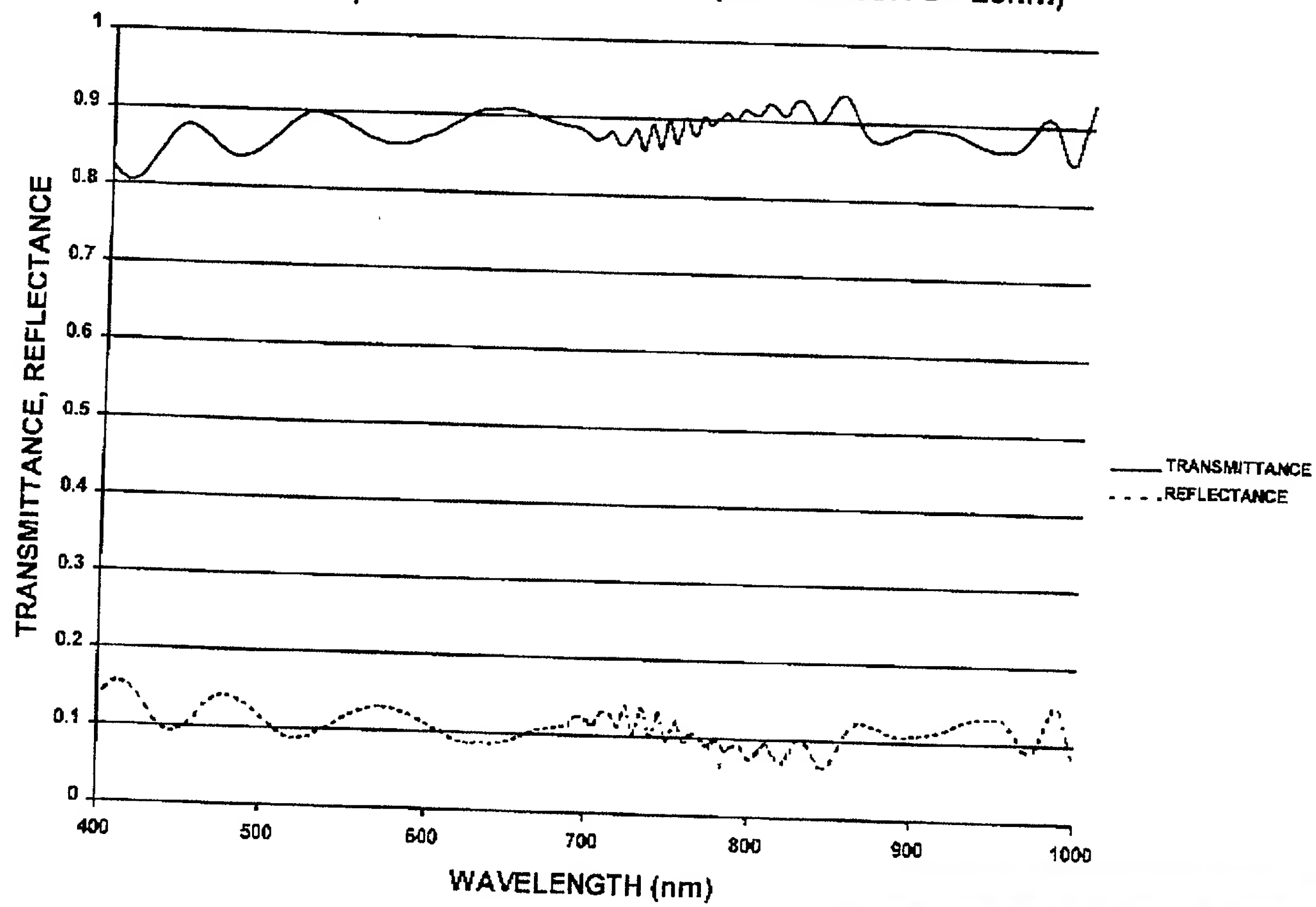
Appendix E

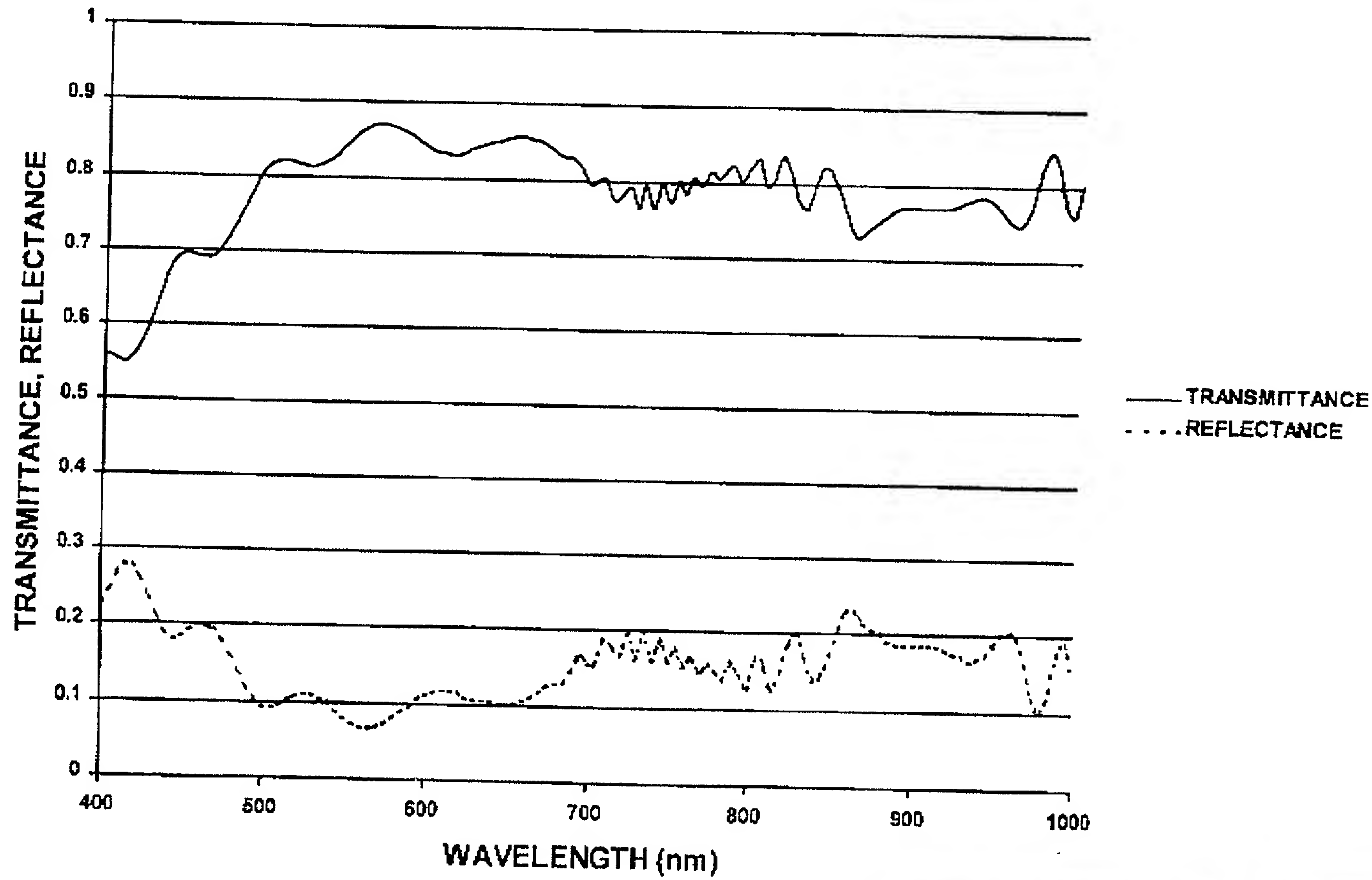
TRANSPARENT BARRIER COATINGS BASED ON ITO FOR FLEXIBLE PLASTIC DISPLAYS

TRANSMITTANCE AND REFLECTANCE OF SEMI-REACTIVELY SPUTTERED ITO ON PET (POLYMER/ITO= 25nm)



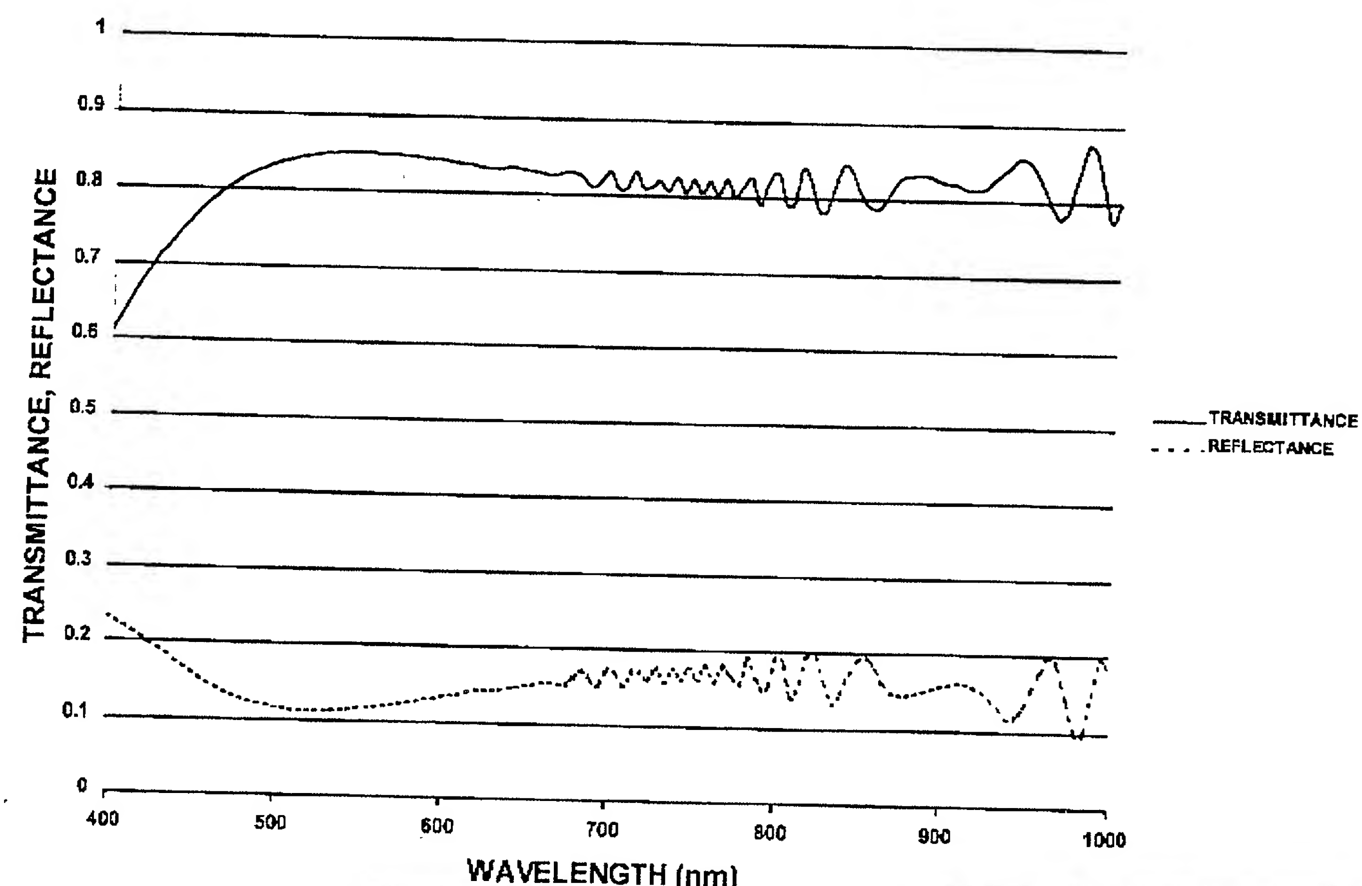
TRANSPARENT BARRIER COATINGS BASED ON ITO FOR FLEXIBLE PLASTIC DISPLAYS

TRANSMITTANCE AND REFLECTANCE OF SEMI-REACTIVELY SPUTTERED ITO ON PET (POLYMER/ITO= 153 nm)



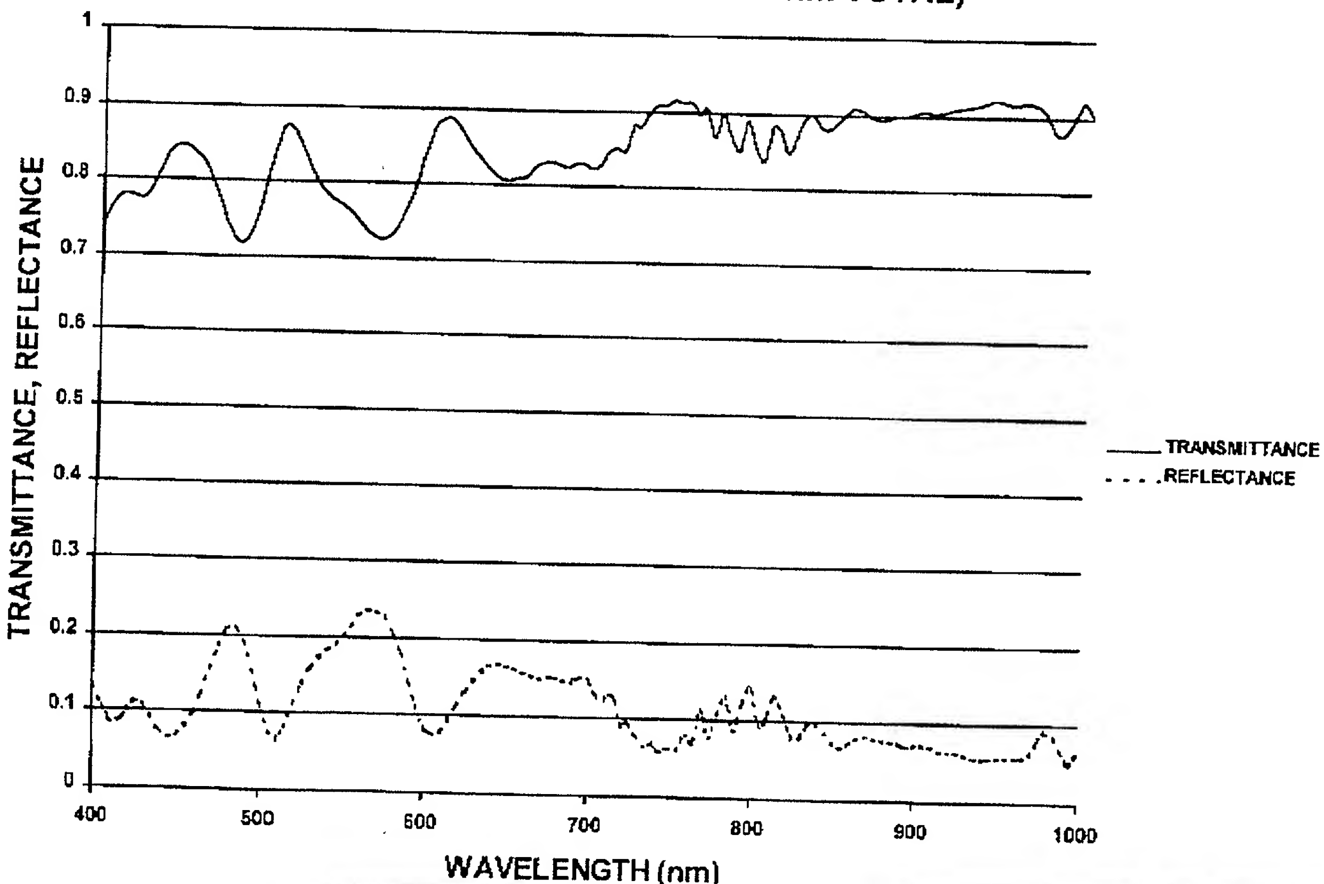
TRANSPARENT BARRIER COATINGS BASED ON ITO FOR FLEXIBLE PLASTIC DISPLAYS

TRANSMITTANCE AND REFLECATNCE OF SEMI-REACTIVELY SPUTTERED ITO ON PET (SINGLE LAYER ITO 134 nm)



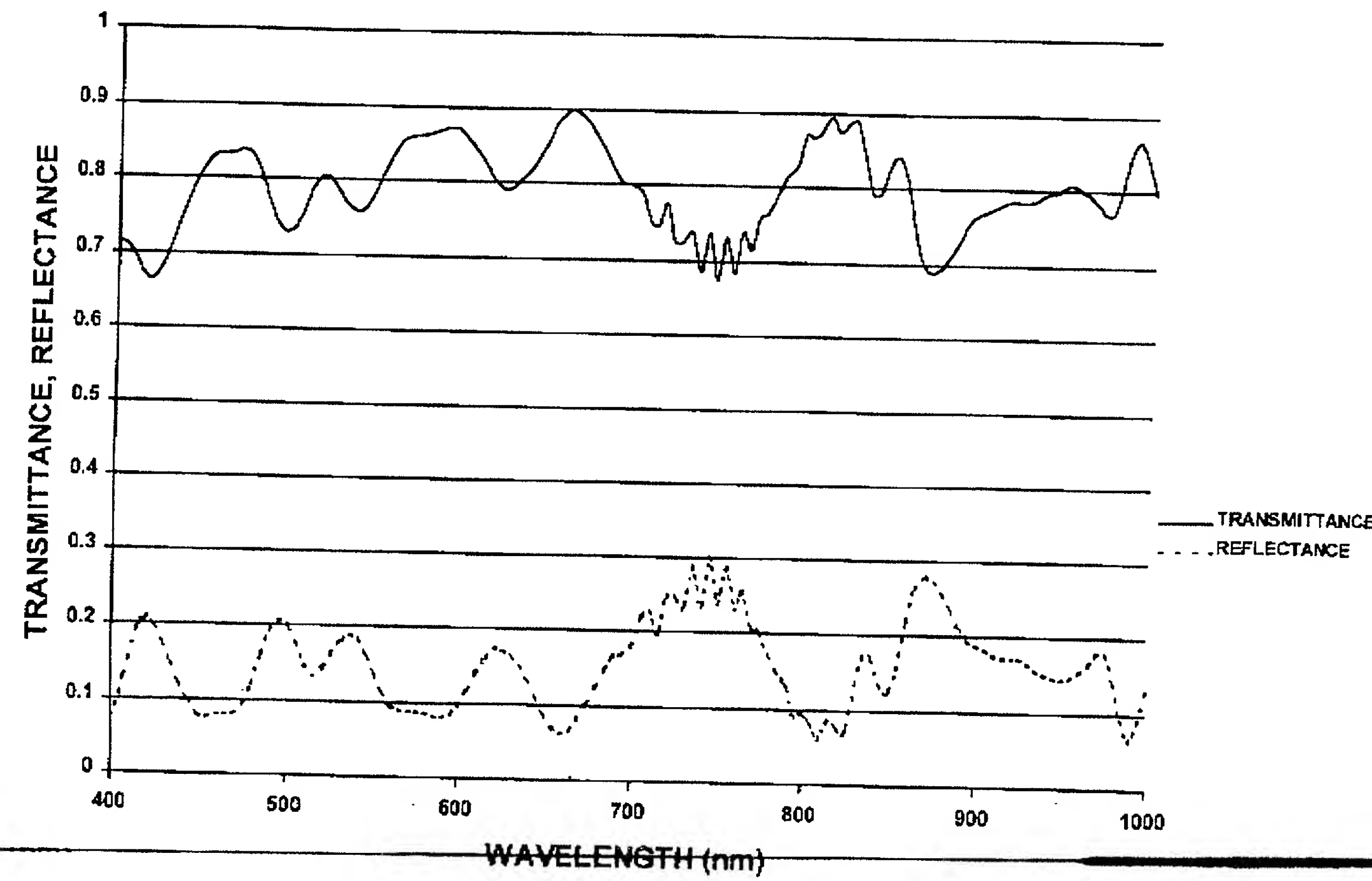
TRANSPARENT BARRIER COATINGS BASED ON ITO FOR FLEXIBLE PLASTIC DISPLAYS

TRANSMITTANCE AND REFLECTANCE OF SEMI-REACTIVELY SPUTTERED ITO/POLYMER ON PET (TWO ITO LAYERS = 50nm TOTAL)



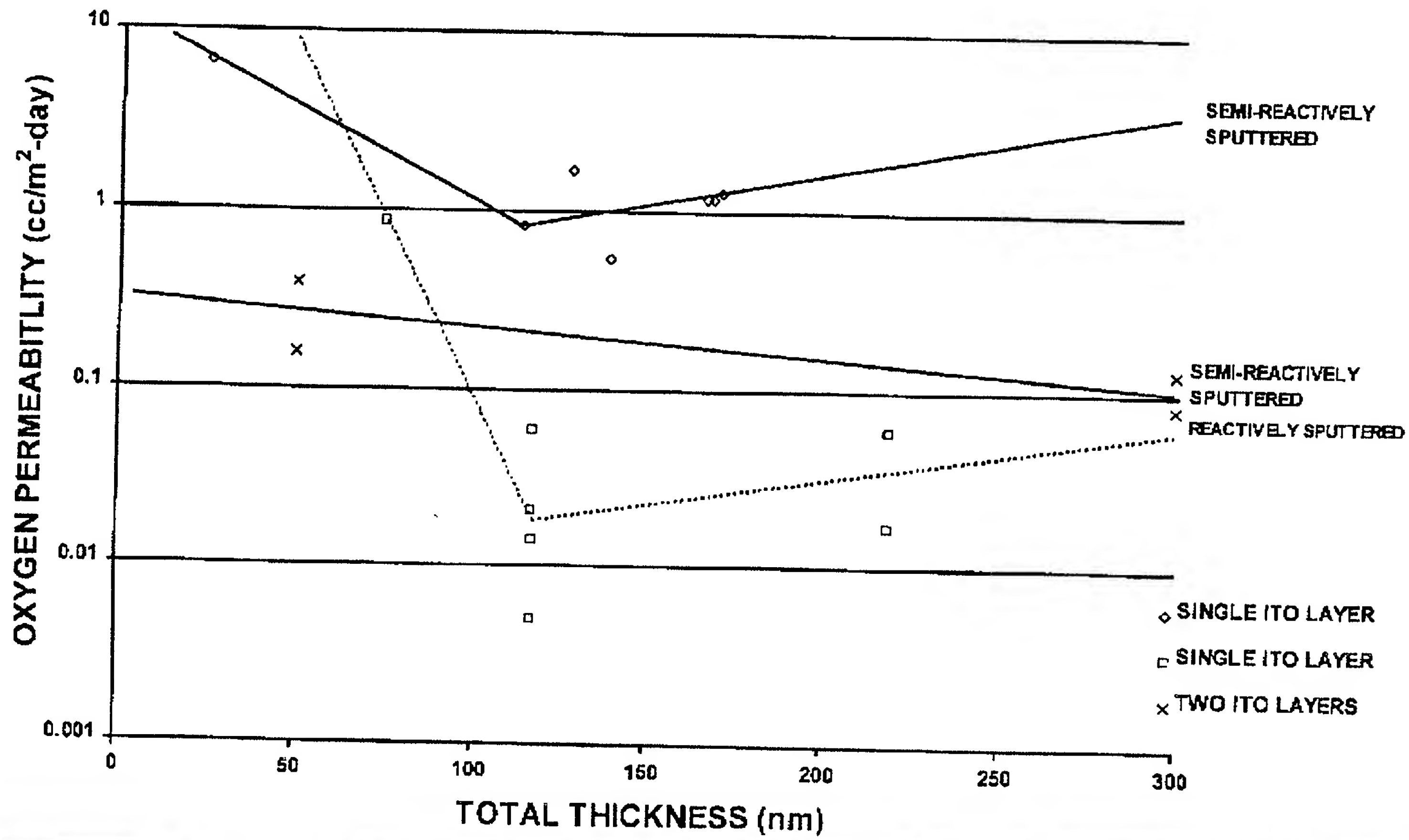
TRANSPARENT BARRIER COATINGS BASED ON ITO FOR FLEXIBLE PLASTIC DISPLAYS

TRANSMITTANCE AND REFLECTANCE OF SEMI-REACTIVELY SPUTTERED ITO POLYMER ON PET (TWO ITO LAYERS = 299nm TOTAL)



TRANSPARENT BARRIER COATINGS BASED ON ITO FOR FLEXIBLE PLASTIC DISPLAYS

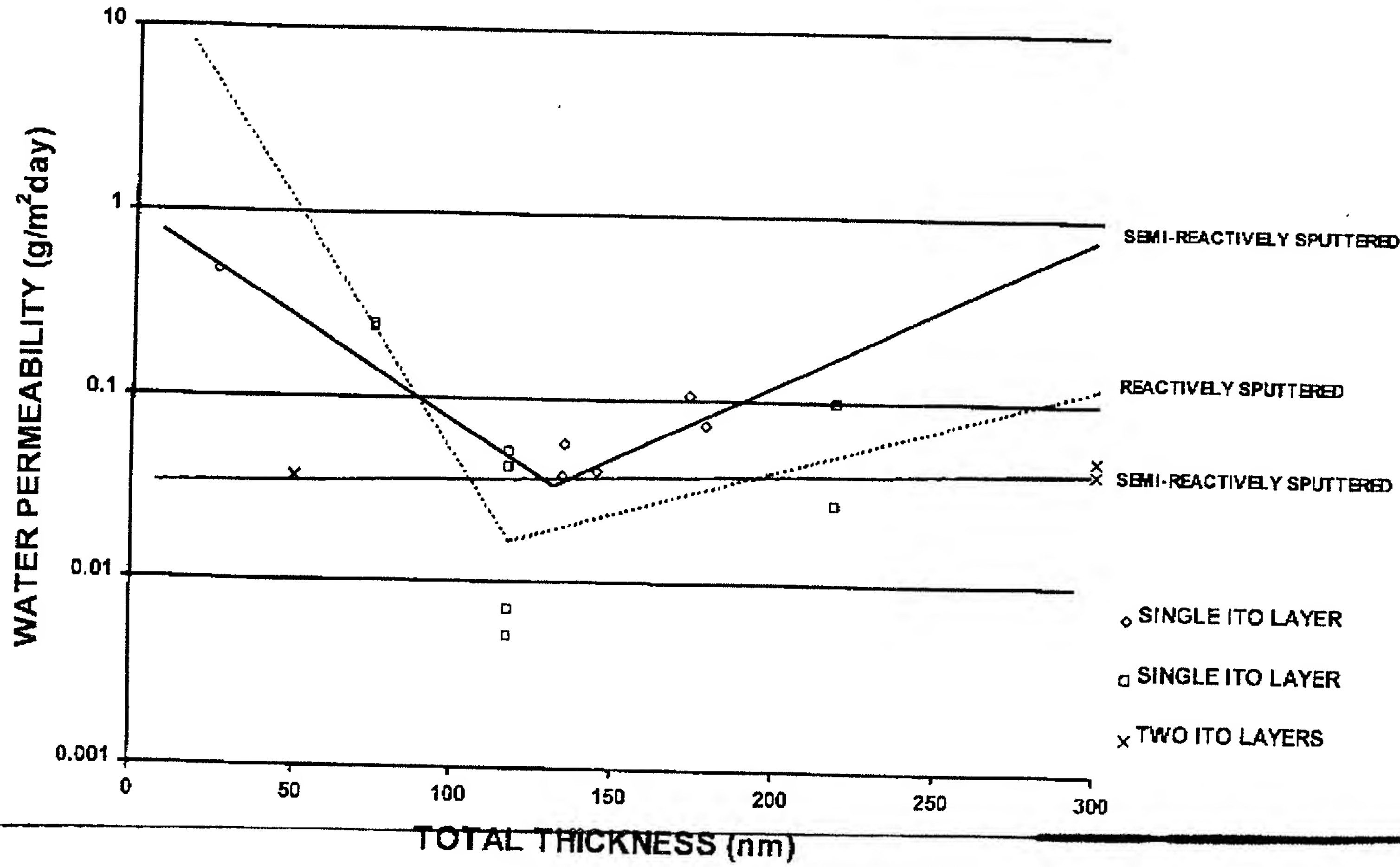
OXYGEN PERMEABILITY VERSUS ITO THICKNESS



Appendix D

TRANSPARENT BARRIER COATINGS BASED ON ITO FOR FLEXIBLE PLASTIC DISPLAYS

WATER VAPORPERMEABILITY VERSUS ITO THICKNESS



TRANSPARENT BARRIER COATINGS BASED ON ITO FOR FLEXIBLE PLASTIC DISPLAYS

Experimental Results For ITO Barriers on PET

Semi-Reactively Sputtered

Total ITO Thickness (nm)	Surface Resistivity (ohms/square)	Rho ($x10^{-4}$ n-cm)	Luminoust (%)	H_2O Permeance (cc/m^2-day)	O_2 Permeance (g/m^2-day)
123.3	38.3	4.685	84	0.038	0.827
172.4	29.9	5.145	82	0.073	1.19
299.2	17.2	5.15	~81	0.049	0.081
49.9	188.4	9.4	~81	0.036	0.156

TRANSPARENT BARRIER COATINGS BASED ON ITO FOR FLEXIBLE PLASTIC DISPLAYS

Experimental Results For ITO Barriers on PET

Semi-Reactively Sputtered

Total ITO Thickness (nm)	Surface Resistivity (ohms/square)	Rho ($\times 10^{-4}$ п-cm)	Luminoust (%)	H_2O Permeance (cc/m^2-day)	O_2 Permeance (g/m^2-day
218.5	31.8	6.94	~80	0.0621	0.038
117.05	57.48	6.64	~82	0.12	0.0246
74.3	348.5	25.6	~86	0.2375	0.8625